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The lognormal distribution of the elements[1]

(A fundamental law of geochemistry and its subsidiary)

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(*Received* 3 *November* 1953)

ABSTRACT

Frequency distribution plots of K, Rb, Sc, V, Co, Ga, Cr, and Zr in Ontario diabase, Sc, V, Ga, Cr, La, and Zr in Canadian granite, K, Rb, and Cs in New England granite and F and Mo in granite from various localities are regular, but assume decided positive skewness when dispersion is large; hence, distribution of concentration is not normal. All distributions become normal, or nearly so, provided the variate (concentration of an element) is transformed to log concentration: this leads to a statement of a fundamental (lognormal) law concerning the nature of the distribution of the concentration of an element in specific igneous rocks.

A subsidiary law concerning the relationship between averages and most prevalent concentrations follows as a direct consequence of the fundamental law.

Dispersions of different elements can be compared and predictions may be made on the basis of the lognormal law. A comparison of the dispersions of elements in igneous rocks and chondrites emphasizes the strikingly high uniformity of abundance of many elements in these meteorites. A given element may show a totally different magnitude of dispersion in different igneous rocks; for example, dispersion of scandium is small in diabase and extreme in granite.

> "The linear scale, since it was first cut on the wall of an Egyptian temple, has come to be accepted by man almost as if it were the unique scale with which Nature builds and works. Whereas, it is nothing of the sort"—(BAGNOLD, 1941)

INTRODUCTION

The accurate determinations of the abundances of the elements is a problem which has concerned us for some time; yet, for one reason or another, the nature of the distribution of the concentrations of the elements in specific rocks and minerals seems to have been overlooked. Many of us, through habit, merely take it for granted that such a distribution is normal, as if the normal law were a law of nature.

"Everybody firmly believes in it because the mathematicians imagine it as a fact of observations and the observers that it is a theory of mathematics" (POINCARÉ, 1892).

This statement made just before the turn of the century is unfortunately still pertinent—though by no means wholly true—despite the accumulation of a vast amount of evidence to show that a normal distribution is in general the exception rather than the rule.

By way of contrast there are those who may feel that the distribution of an element is likely to be so complex and irregular in geological materials that the mathematical handling of the observations would be almost hopelessly difficult and of little or no practical significance.

[1] Most of the information given and discussed here is from investigations which have had support from the Office of Naval Research, Washington.

[2] Now at Department of Geology and Mineralogy, Oxford.

In this paper an attempt will be made to show first, that the distribution of the concentration of an element in a specific rock type is not normal, and second, that it is nevertheless simple and easily handled.

CHOICE OF DATA

The principal discussion is restricted to two specific common igneous rocks, granite and diabase. For a statistical investigation of this type, the very nature of the material itself immediately poses problems—should for example, all types of diabase be included (olivine-bearing to granophyric varieties); how fresh should they appear to be; how large a geographical distribution should be represented; how many specimens from each locality; should unusual types be included, and so on? The problem of granite itself is enough to introduce several other problems. No attempt will even be made to begin to answer these questions and the choice of data is fortunately, perhaps, dictated almost solely by what is currently available.

Nearly all emphasis will be placed on the rarer elements, mainly because of their ability to show a large variation* of concentration in a specific rock type and partly because available data on them are particularly satisfactory. The concentration of a common constituent such as silicon is unable to vary widely in a given rock type, because if it did we pass by definition on to some other rock type. It does not follow that a rare element is bound to show a large dispersion in a specific rock type: its low abundance merely provides it with the freedom to vary its concentration widely should its properties happen to be such that they will tend to cause it to do so. For the statistical purposes of this investigation it should be recalled that observations which show a large dispersion about some central value are far more sensitive indicators of the nature of a distribution than those which show a small dispersion.

Thirteen elements (K, Rb, Cs, F, Sc, Zr, Cr, Co, La, Pb, Mo, Ga, and V) will be discussed. They cover a wide range of chemical properties: most are lithophile, a few are both lithophile and chalcophile; one (fluorine) is a non-metal and two (zirconium and chromium) readily form discrete minerals (zircon and chromite, respectively) even when present at comparatively low concentrations. Such a variety of elements is included because of the possibility that distinct types may show different types of distribution. The total abundance range varies by a factor of about 35,000; from 1 ppm (Mo in granite) to 35,000 ppm (K in granite).

The principal sources of data are as follows: all elements in diabase (FAIRBAIRN, AHRENS and GORFINKLE, 1952); Rb and K in granite (AHRENS, PINSON and KEARNS, 1952); F in granite (SERAPHIM, 1951); Mo in granite (SANDELL, 1953) other elements in granite (unpublished data of AHRENS and GORFINKLE—given below as Table 1). Some sources of information on chondrites will be listed because the amount of dispersion of a few elements in the commonest meteorites will be compared with that in diabase and granite; for Rb and K (AHRENS, PINSON and KEARNS, 1952); Li, Sc, Sr, Ba and Zr (PINSON, AHRENS and FRANCK, 1954) and Mo (SANDELL, 1953) and for other constituents (UREY and CRAIG, 1953).

* On a geometric and not a linear scale.

With the exception of molybdenum, each element in granite and diabase has been determined spectrochemically (in duplicate) by methods described by AHRENS (1954). Each such determination has been calibrated in terms of its recommended value (AHRENS, 1954, Chap. 4) in the standard rocks, granite G–1 and diabase W–1 (FAIRBAIRN *et al.*, 1951) so as to reduce the amount of possible systematic error as far as possible. The presence of systematic error would not influence the conclusions which will be made about the distribution of concentration but for the purpose of abundance calculations such error should naturally be at a minimum.

Only the most satisfactory of the spectrochemical data have been used. Thus Sr and Ba were determined visually, and as accuracy is therefore inferior, these two elements are omitted. Determinations of Pb and Ag are of poor quality in diabase as their concentrations usually border on detection limits. Cu determinations have been omitted because of fairly frequent self-absorption by the copper analysis lines. There are, of course, innumerable other published determinations of most of the above elements in granite, diabase and chondrite, but only those referred to here will be used for these reasons: first, each constituent has been determined by one method in one laboratory, second, many published determinations of the rarer elements are reported as semi-quantitative and are hence unsuitable, and third, for some constituents the number of specimens of a specific rock type which have been analyzed is far too small for statistical purposes.

The principal locality sources for each rock type are as follows:

granite—Cs, Rb and K. Calk-alkaline granites of New England. (See CHAYES, 1952, for discussion and for earlier references to the New England granites.)

—Ga, Cr, Sc, La, V, Pb and Zr. A variety of types from Ontario. (See Appendix for locality details and JOHNSTON, 1949, and BELL, 1953, for some descriptive details.)

—F (SERAPHIM, 1951) and Mo (SANDELL, 1953) have been determined in granites from a wide variety of sources.

diabase—pre-Cambrian diabase from Ontario (Nipissing, Nipigon and Matachewan) as indicated by Fig. 1 of FAIRBAIRN, AHRENS and GORFINKLE (1953). A fairly wide variety of types is represented.

The discussions on granite and diabase which follow are based on a total of 812 observations. The average number of observations per constituent is about 40; for a few elements it is a little less than 30 and for some the number of observations is about 60. These are not large numbers, particularly as some elements show enormous dispersion, and in some respects this investigation can only be viewed as a modest beginning. Nevertheless, it will become apparent that some interesting and emphatic conclusions emerge from the data which are now at hand.

Two lots of data which have not been elsewhere available are, first, caesium in New England granite, and second, several elements in Canadian granite.

The determinations of several elements in Canadian granite appear below as

Table 1. The caesium values (in ppm) for each of the specimens listed in Table 1 of Ahrens, Pinson and Kearns (1952), and in the order given there (Sample 2A4 to G–1) are: n.d.*, 1·3, 1·9, n.d., 10, 14, 19, 9, 4, 4, 4, 3·7, 2·3, 3, 2·6, 4·5, 11, 3·7, 10, 7, 16, 4, 8, 13·5, 2·8, 2·3, 6·8, 4·2, n.d., 4 and 2·5.

Table 1. Ga, Cr, Sc, La, V, Pb and Zr in Canadian granite

Sample No.†	*Ga ppm*	*Cr ppm*	*Sc ppm*	*La ppm*	*V ppm*	*Pb ppm*	*Zr ppm*
G–1	19	22	3	170	21	24	220
KB–1	16	40	12	49	75	39	200
KB–2	14	30	6	32	43	9	130
KB–3	15	120	24	59	200	17	180
KB–4	21	25	10	15	50	11	120
KB–5	16	3·5	2	44	7·5	22	150
KB–6	16	5·3	16	74	30	14	410
KB–7	16	5·8	60	89	33	10	200
KB–8	19	17	4	33	27	26	100
KB–9	16	22	6	86	34	20	250
KB–10	22	410	5	74	42	14	160
KB–11	16	2	2·3	140	10	~2	180
KB–12	22	24	6	67	52	20	160
KB–13	15	15	7	49	51	9	190
KB–14	20	35	15	110	82	29	270
KB–15	18	28	6	33	630	8	140
KB–16	14	95	28	50	144	8·5	160
KB–17	17	59	12	52	94	7·5	160
KB–18	15	38	13	64	94	6	180
KB–19	13	17	3	57	29	12	180
48–63		19			8		100
48–115		7	~1	33	11		150
48–158		3	~1		5·5		80
48–188		6	3·7	52	23		220
48–407	16					68	
48–411	15					8·5	
48–421	14					15	
48–422	22					10	
48–472	15					6	
48–476	14					5·5	
48–485		5·5	2·3		19		150
48–489		27	1·3	13	7		110
48–490		2	~1		5·6		50
48–494	19					3·8	
48–495	13					6·5	
48–496	16					8	
48–510 → 17	17					18	
48–518 → 20	19					9	
48–521, 2	13					7·7	

* Not determined.
† See Appendix for locality details.

Frequency Distribution Diagrams

The distribution of the ratio of closely associated rubidium and thallium has been shown to be lognormal* in potassium minerals as a whole (Ahrens, 1948). Further indications that the concentrations of elements might follow this type of distribution in geological materials comes from Ahrens and Gorfinkle (1950) who found zirconium lognormally distributed in Ontario diabase and Krige (1952) and Sichel (1952) who observed that gold followed a like distribution in gold-bearing sediments of the Witwatersrand System, Transvaal, South Africa.

In the frequency distribution diagrams which follow (Figs. 1–20) both concentration and log concentration are used as variates for each element. Because of the large variation in the abundance (significant for linear plots only) and amount of dispersion shown by each element, various intervals have been chosen. These are so chosen that observations occur in at least five of them, but not in an exceptionally large number. Gallium (Fig. 1) with four intervals is exceptional because of its extremely small dispersion. Figs. 1–20 are arranged approximately in order of increasing dispersion.

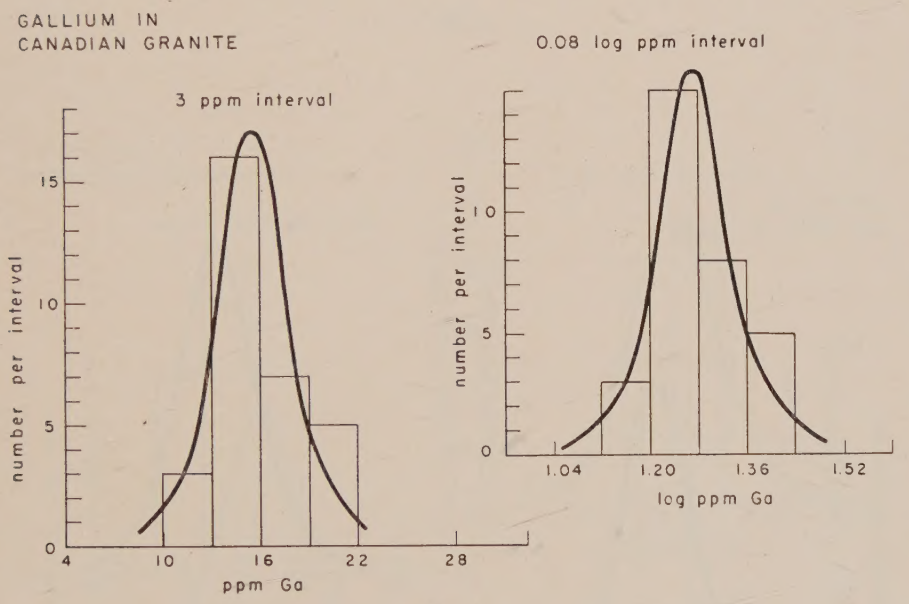

Fig. 1

* The distribution of x is lognormal when the distribution of log x is normal (see Gaddum, 1945, for discussion and examples of this distribution).

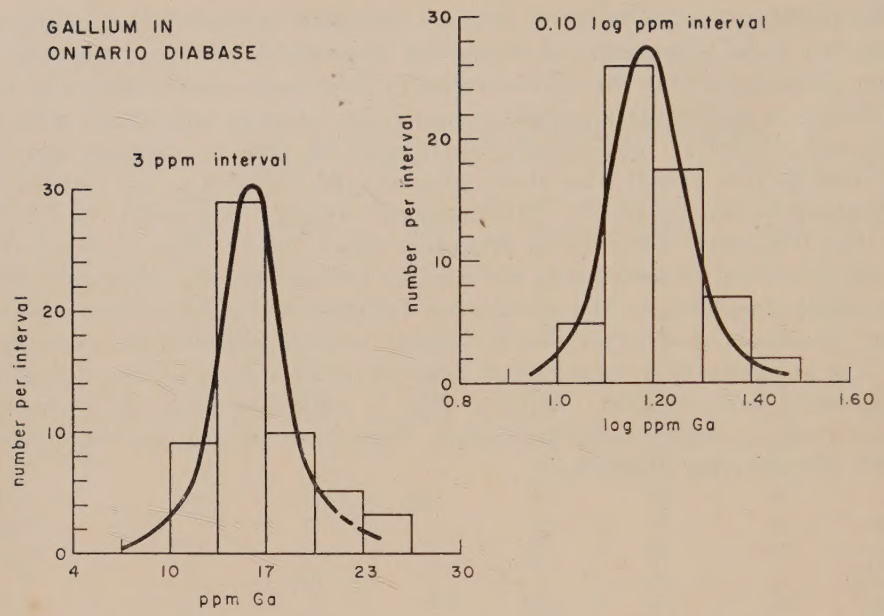
GALLIUM IN
ONTARIO DIABASE
3 ppm interval
number per interval
ppm Ga
0.10 log ppm interval
log ppm Ga

Fig. 2

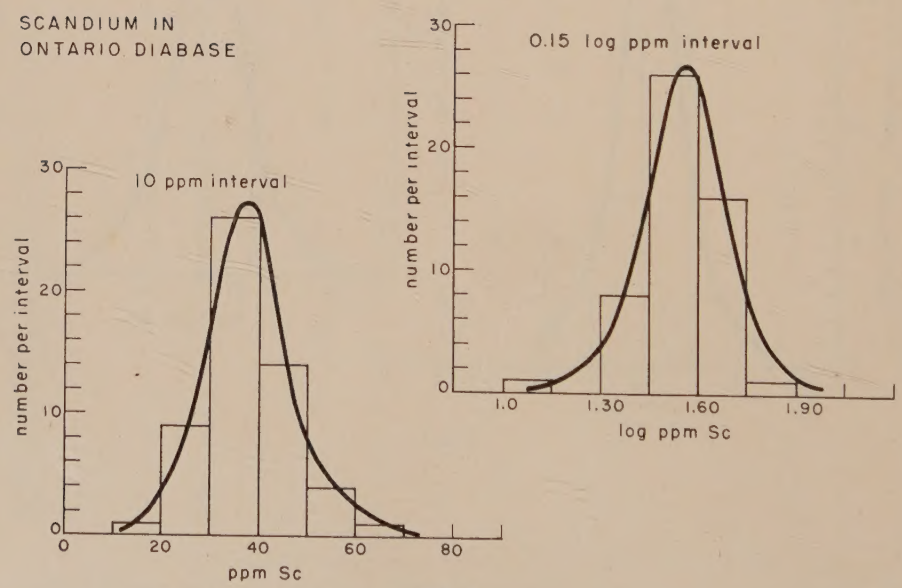
SCANDIUM IN
ONTARIO DIABASE
10 ppm interval
number per interval
ppm Sc
0.15 log ppm interval
log ppm Sc

Fig. 3

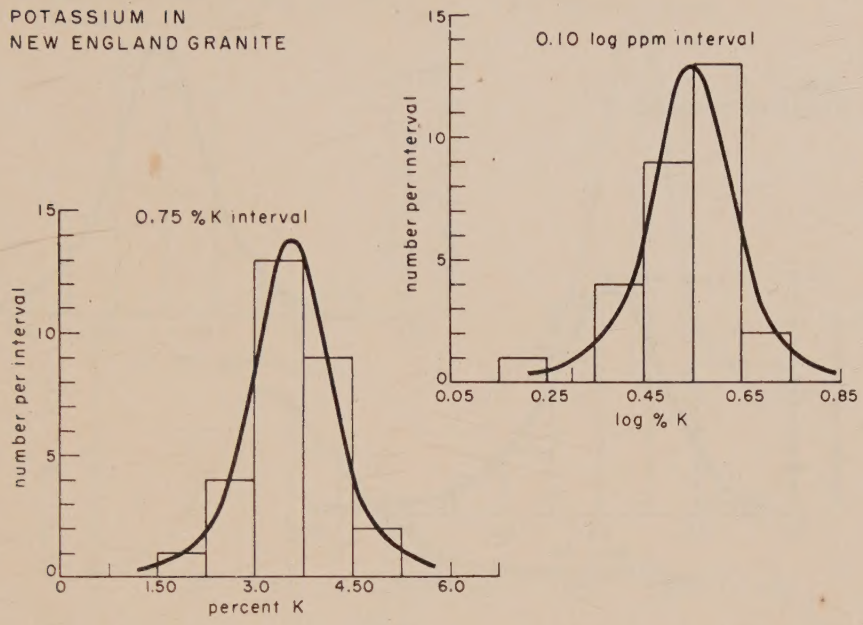
POTASSIUM IN
NEW ENGLAND GRANITE
0.75 % K interval
number per interval
percent K
0.10 log ppm interval
log % K

Fig. 4

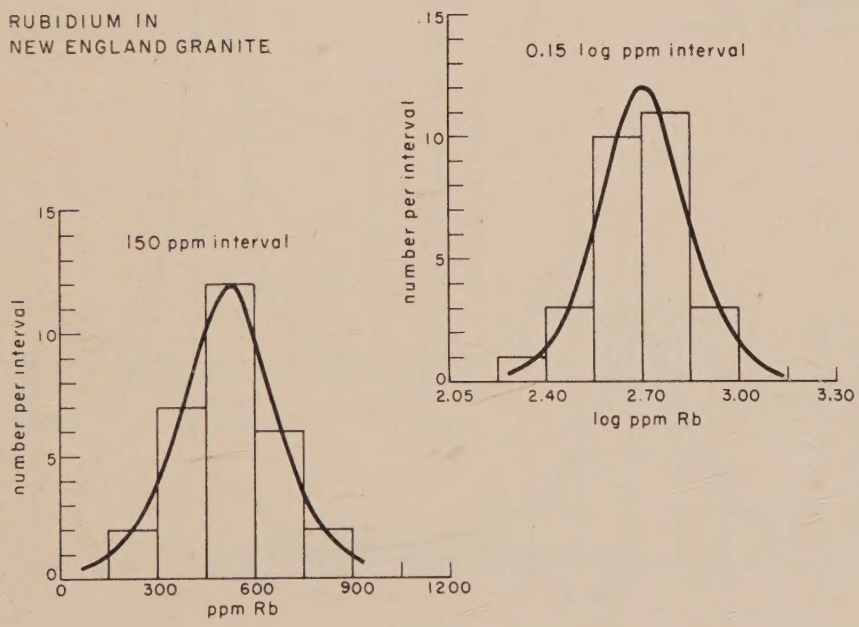
RUBIDIUM IN
NEW ENGLAND GRANITE
150 ppm interval
number per interval
ppm Rb
0.15 log ppm interval
log ppm Rb

Fig. 5

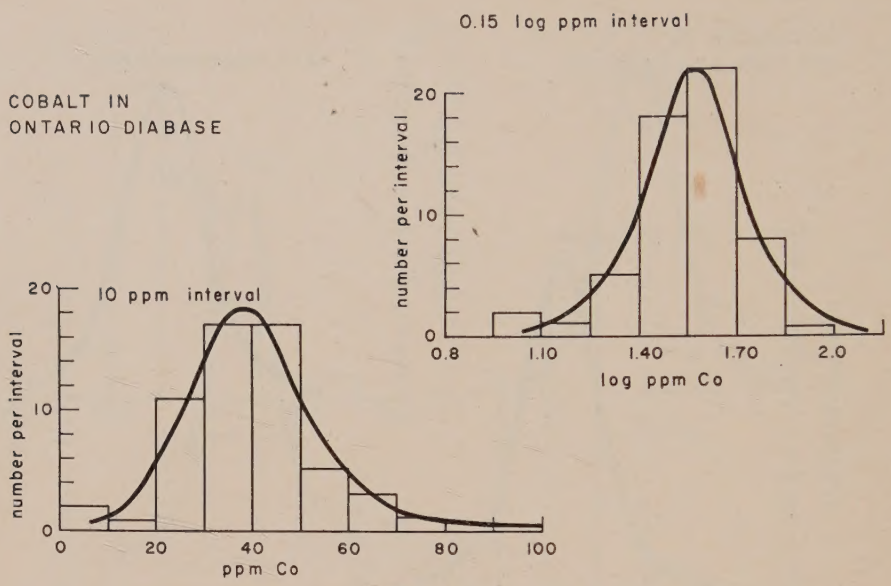
COBALT IN
ONTARIO DIABASE
0.15 log ppm interval
number per interval
log ppm Co
10 ppm interval
ppm Co

Fig. 6

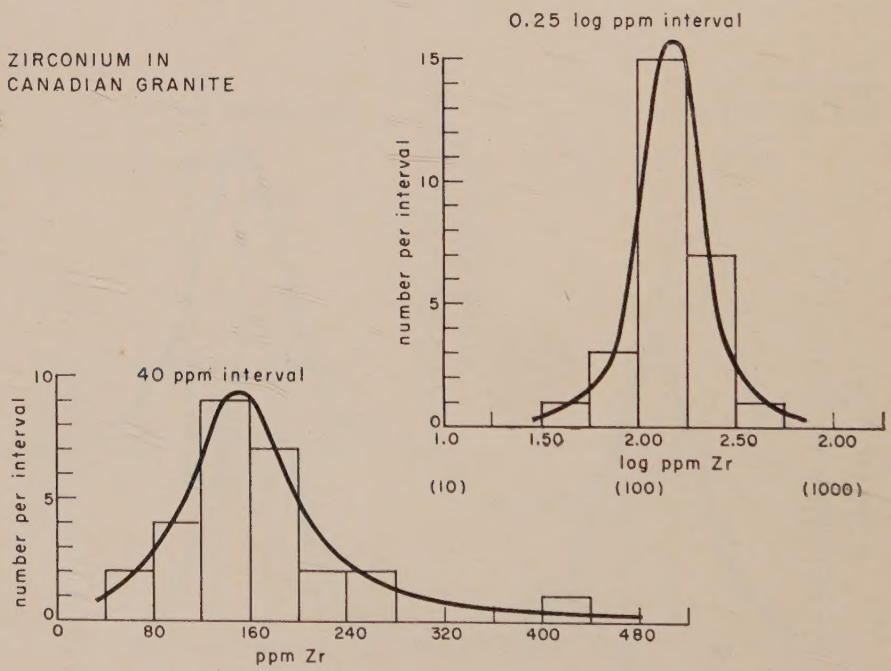
ZIRCONIUM IN
CANADIAN GRANITE
0.25 log ppm interval
number per interval
log ppm Zr
(10)
(100)
(1000)
40 ppm interval
ppm Zr

Fig. 7

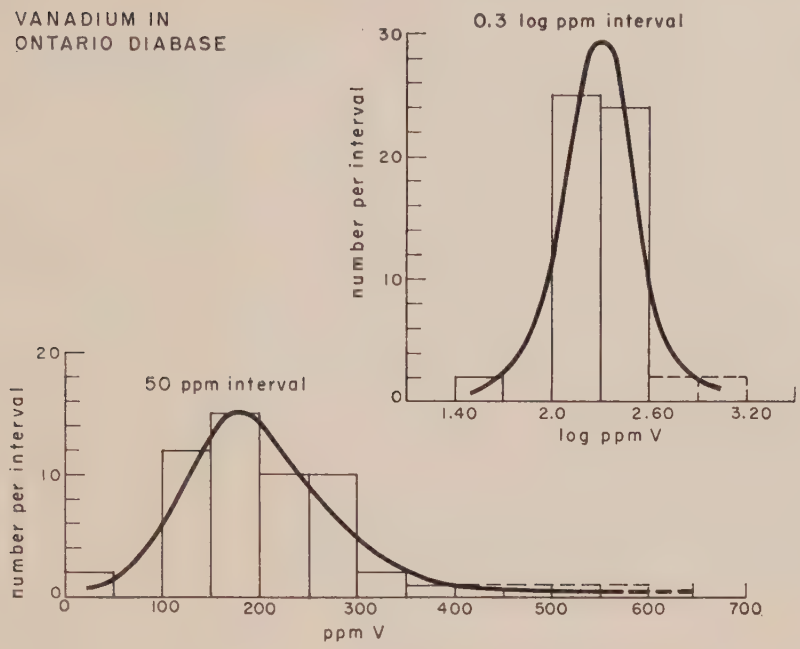
VANADIUM IN
ONTARIO DIABASE
0.3 log ppm interval
number per interval
30
20
10
0
1.40
2.0
2.60
3.20
log ppm V
50 ppm interval
number per interval
20
10
0
0
100
200
300
400
500
600
700
ppm V

Fig. 8

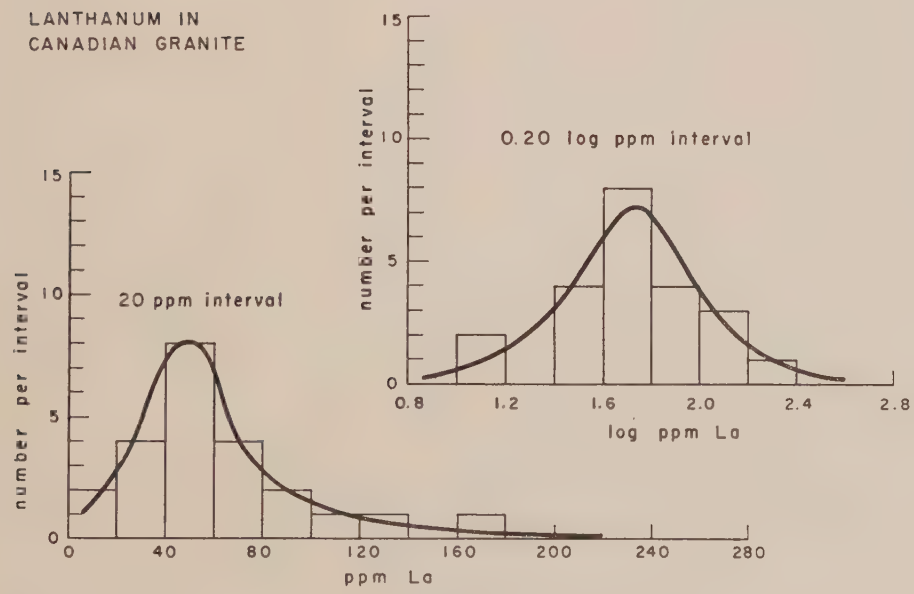
LANTHANUM IN
CANADIAN GRANITE
0.20 log ppm interval
number per interval
15
10
5
0
0.8
1.2
1.6
2.0
2.4
2.8
log ppm La
20 ppm interval
number per interval
15
10
5
0
0
40
80
120
160
200
240
280
ppm La

Fig. 9

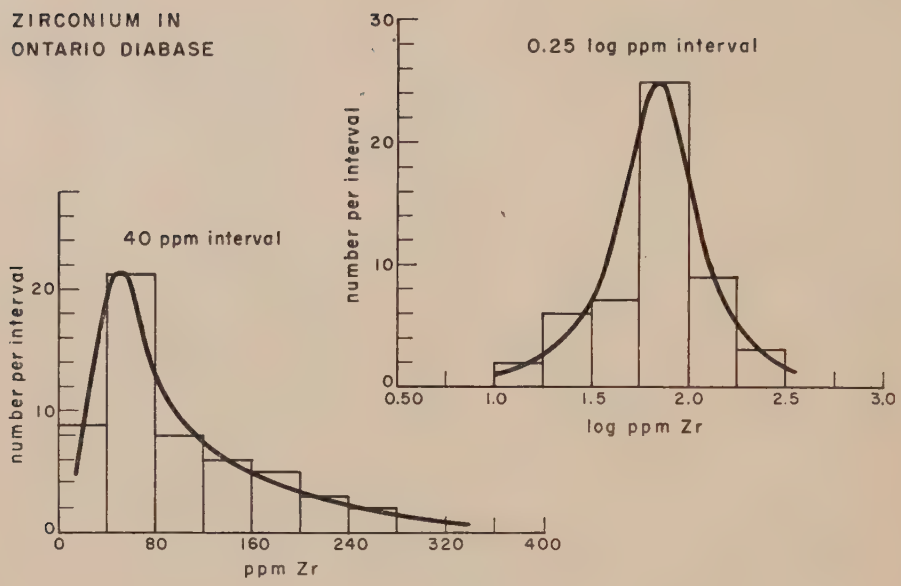
ZIRCONIUM IN
ONTARIO DIABASE
40 ppm interval
number per interval
ppm Zr
0.25 log ppm interval
log ppm Zr

Fig. 10

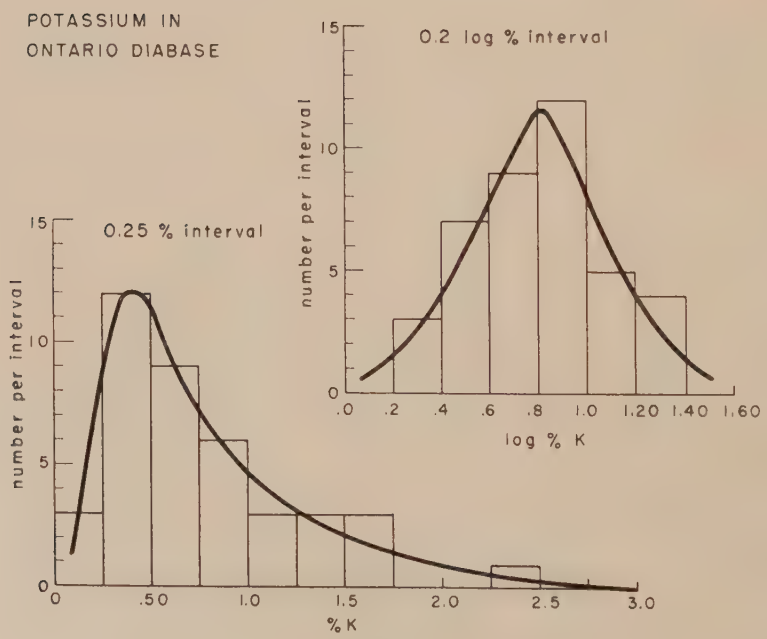
POTASSIUM IN
ONTARIO DIABASE
0.25 % interval
number per interval
% K
0.2 log % interval
log % K

Fig. 11

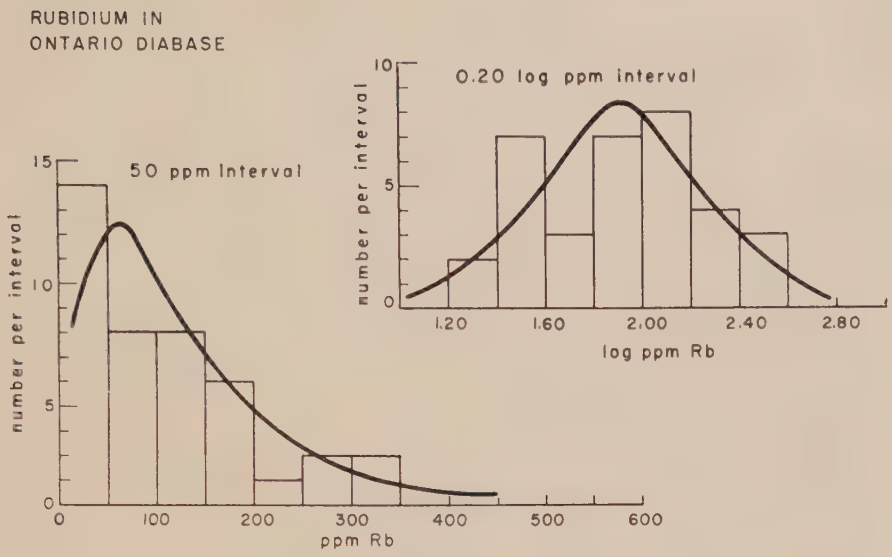
RUBIDIUM IN
ONTARIO DIABASE
50 ppm Interval
number per interval
ppm Rb
0.20 log ppm interval
log ppm Rb

Fig. 12

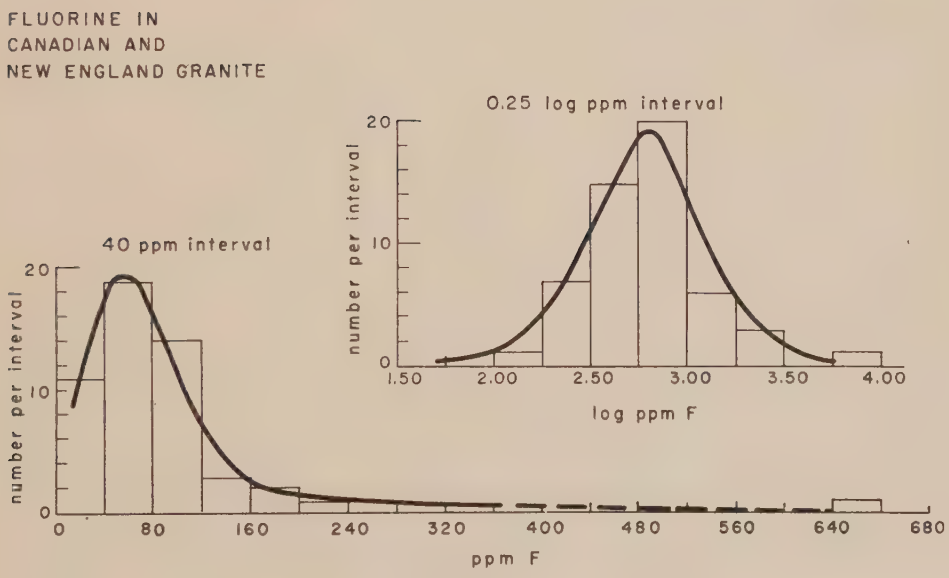
FLUORINE IN
CANADIAN AND
NEW ENGLAND GRANITE
40 ppm interval
number per interval
ppm F
0.25 log ppm interval
log ppm F

Fig. 13

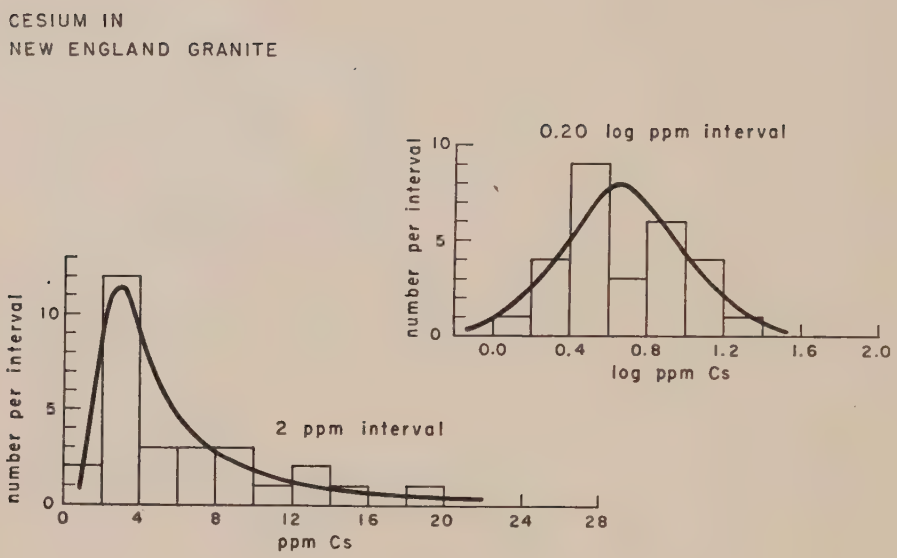
CESIUM IN
NEW ENGLAND GRANITE
0.20 log ppm interval
number per interval
log ppm Cs
2 ppm interval
ppm Cs

Fig. 14

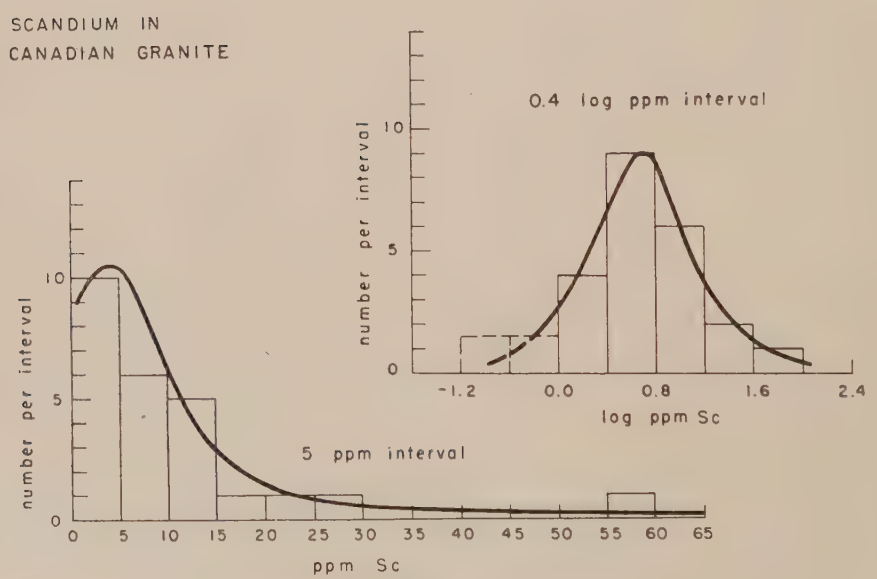
SCANDIUM IN
CANADIAN GRANITE
0.4 log ppm interval
number per interval
log ppm Sc
5 ppm interval
ppm Sc

Fig. 15

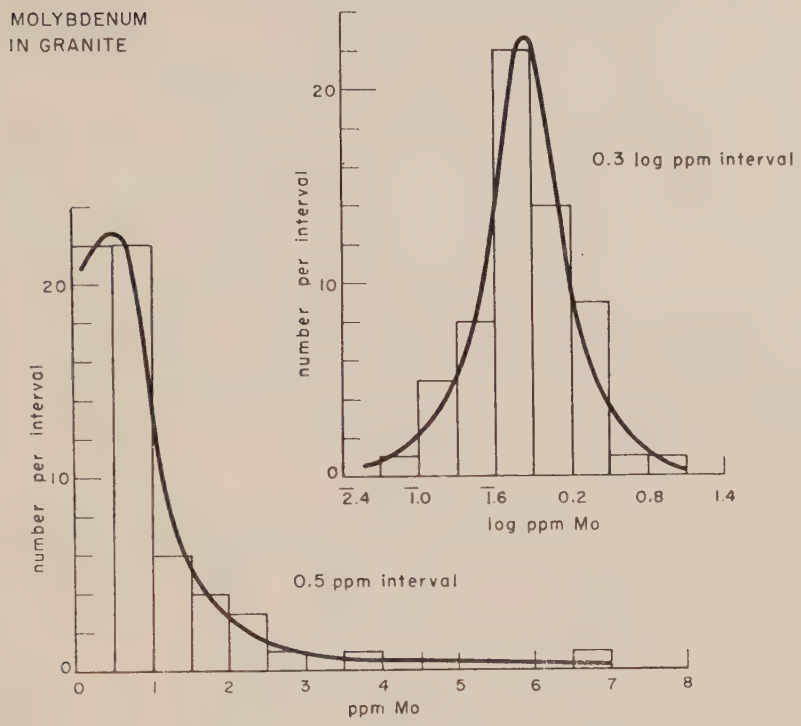
MOLYBDENUM
IN GRANITE
0.3 log ppm interval
number per interval
log ppm Mo
0.5 ppm interval
ppm Mo

Fig. 16

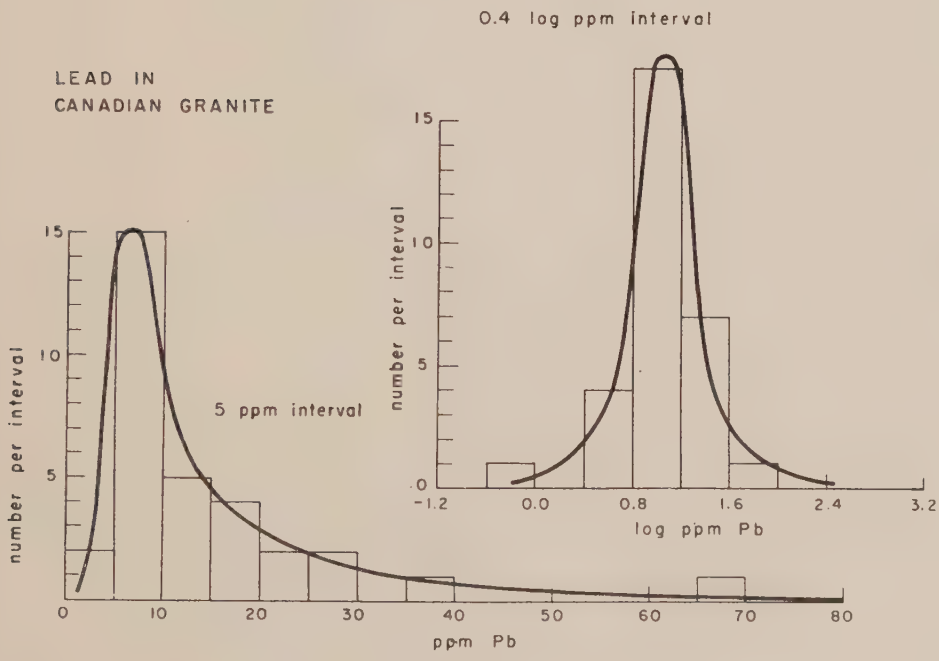
0.4 log ppm interval
LEAD IN
CANADIAN GRANITE
5 ppm interval
number per interval
log ppm Pb
ppm Pb

Fig. 17

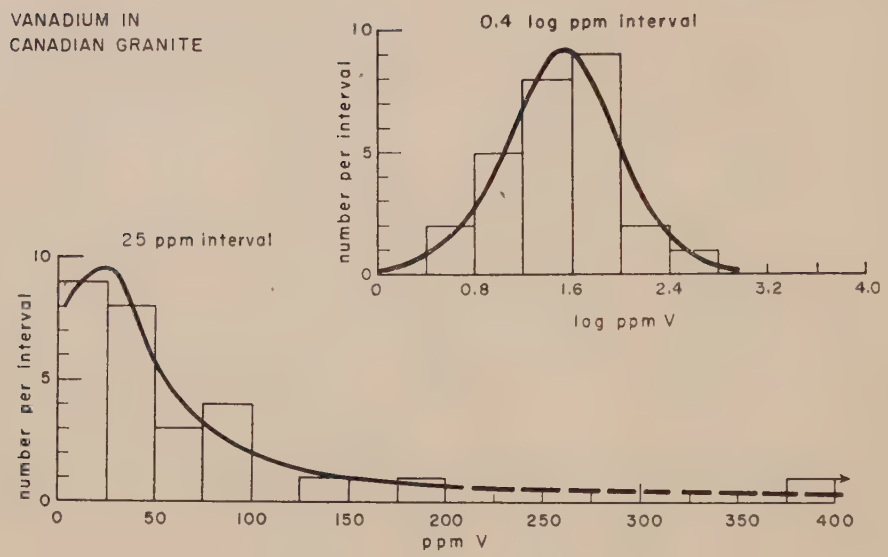

Fig. 18

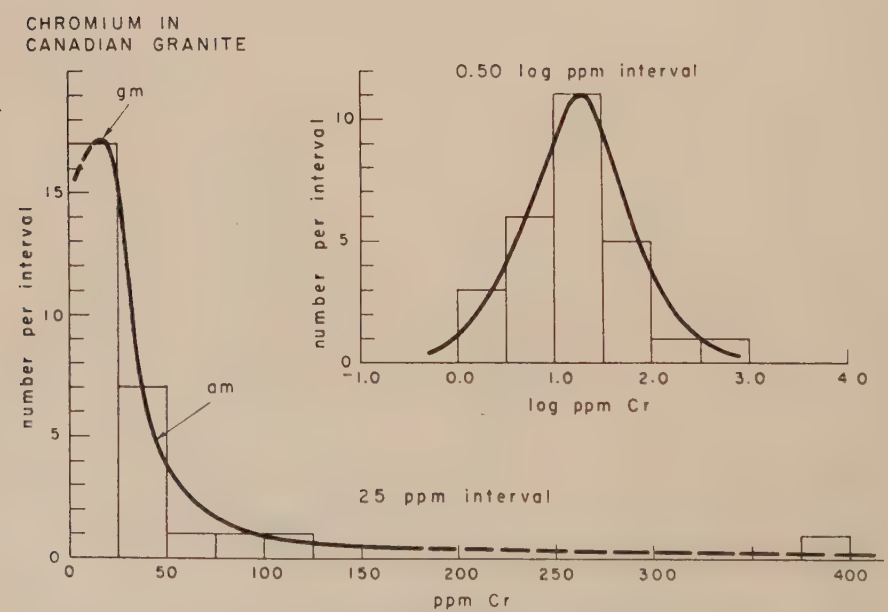

Fig. 19. Arithmetic mean (am) and geometric mean (gm) are indicated. (See discussion on abundance and most prevalent concentrations.)

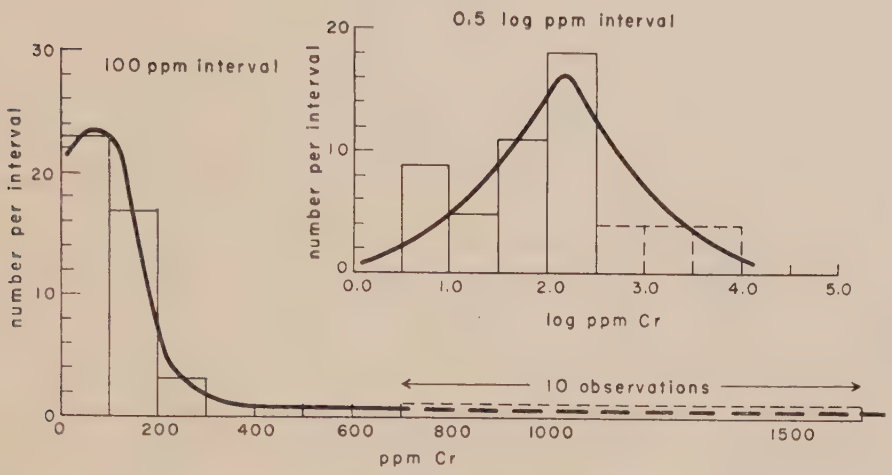

Fig. 20

A Fundamental Law of Geochemistry

Distributions with concentration as variate are discussed first, followed by those with log concentration as variate.

Elements with small dispersion (Ga (d* and gr*), Sc(d), K(gr) and Rb(gr)) appear to be normally distributed whereas signs of positive skewness appear in Zr(gr), V(d), and La(gr). Well developed and unmistakable positive skewness is clear in Zr(d), K(d), Rb(d), F(gr), Cs(gr), Sc(gr), Mo(gr), Pb(gr), V(gr), Cr(gr) and Cr(d): a large dispersion is shown by all of these elements (see discussion and Table 2).

The development of positive skewness at moderate to large dispersions leads to the definite conclusion that the distribution of concentration is not normal. The fact that elements with small dispersion (Ga, etc.) appear to be normally distributed is insignificant. The magnitude of their dispersion is so small that many hundreds of determinations of exceptional accuracy would have to be made in order to reveal the nature of the dispersion; hence we look to elements showing large dispersion to provide this information.

Each plot of log concentration shows, or at least very closely approaches, a lognormal distribution whether dispersion is large or small. Irregularities of detail are bound to appear (Cs(gr) and Cr(d) are examples) because the number of observations for each example is only moderate. Spectrochemical determinations of Cr in diabase above ~700–800 ppm are approximate because of excessive line blackening; the ten such determinations are indicated in Fig. 20. The fact that these ten determinations are only semi-quantitative is not particularly significant as is evident from Fig. 20.

* Diabase and granite.

V. M. Goldschmidt has defined one principal task of geochemistry as, "to find the laws of distribution of the elements." As the total number of observations referred to in this paper is reasonably large (812) and as they refer to a variety of elements, we may restate the above general conclusion as a fundamental law

Table 2. Statistical information on some elements in granite and diabase

Element	λ	λ'	C (%)	*Arithmetic mean (am)*	*Geometric mean (gm)*	$\frac{am}{gm}$
Ga (d)	0·07	1·17	15	17 ppm	17 ppm	1·0
Ga (gr)	0·07	1·17	15	17 ppm	17 ppm	1·0
Sc (d)	0·12	1·32	25	37 ppm	36 ppm	1·03
K (gr)	(0·13)*	(1·35)	(25)	3·5%	3·5%	1·00
Rb (gr)	0·14	1·36	28	520 ppm	520 ppm	1·00
Co (d)	0·17	1·48	33	40 ppm	35 ppm	1·13
Zr (gr)	0·18	1·50	28	170 ppm	165 ppm	1·03
V (d)	0·22	1·70	45	220 ppm	210 ppm	1·05
K (d)	0·28	1·80	60	0·8%	0·68%	1·18
La (gr)	0·28	1·90	60	63 ppm	54 ppm	1·17
Zr (d)	0·30	2·0	60	100 ppm	80 ppm	1·25
Cs (gr)	0·30	2·0	70	6·5 ppm	5 ppm	1·30
Pb (gr)	0·32	2·1	70	15 ppm	12 ppm	1·25
F (gr)	0·37	2·3	100	800 ppm	500 ppm	1·6
Rb (d)	0·38	2·4	80	110 ppm	83 ppm	1·32
Mo (gr)	0·42	2·6	100	1·1 ppm	0·75 ppm	1·47
Sc (gr)	0·48	3·0	115	11 ppm	5 ppm	2·2
V (gr)	0·50	3·2	>150	67 ppm	32 ppm	2·1
Cr (gr)	0·54	3·5	>150	40 ppm	17 ppm	2·35
Cr (d)	0·73	5·6	>150	220 ppm	93 ppm	2·40

concerning the nature of the distribution of the concentration of an element, namely; *the concentration of an element is lognormally distributed in a specific igneous rock.*

It is not at all unlikely that this law may be found to hold fairly generally, as for example in specific minerals (an example is given below) and in some sediments† (Kirge, 1952; Sichel, 1952). A restatement of the law in more general terms could be made if many examples of lognormal distribution were to be found in a variety of environments.

Dispersion and Predictions

Dispersion may be accurately calculated and compared and predictions can be made once the nature of a distribution has been established. As the logarithm of

* Based on observations from other sources as well.

† The frequency distribution plot of Sr in limestone (Kulp, Turekian, and Boyd, 1952) is regular and shows decided positive skewness suggesting lognormal distribution.

the concentration of an element is normally distributed in a specific igneous rock use may be made of the relationship of the familiar form,

$$\lambda = \pm\sqrt{\frac{\Sigma {d_L}^2}{n-1}}$$

to determine and express its dispersion. λ (GADDUM, 1945) is the standard deviation of the log values and d_L, the deviation of the logarithm of an observation from the arithmetic mean ($\bar{x}_L$) of all log observations; n is the number of observations. The geometric mean (see below), the nth root of the product of n observations, is given by the antilog of $\bar{x}_L$.

It will be recalled that normal law predicts that two thirds of all observations should fall within $\bar{x}_L + \lambda$ and $\bar{x}_L - \lambda$, and 95% within $\bar{x}_L + 2\lambda$ and $\bar{x}_L - 2\lambda$.

Consider the example of vanadium in Canadian granite (Table 2). The arithmetic mean of the log values ($\bar{x}_L$) and λ calculate as 1·50 and 0·50, respectively. Hence, the limits within which two-thirds of all the observations should fall are, 1·50 + 0·50 = 2·00 and 1·50 − 0·50 = 1·00, respectively. From the antilogs of 1·50, 2·00 and 1·00, we have 32 ppm V (geometric mean), 100 ppm V (upper limit) and 10 ppm V (lower limit). The 95% limits should be, $1{\cdot}50 \pm 2\lambda = 2{\cdot}50$ and 0·50, the antilogs of which are 320 ppm V (upper limit) and 3·2 ppm V (lower limit).

Although λ is calculated with the aid of logarithms and is usually used as a measure of dispersion in lognormal distributions, it may be more satisfactory to use its antilog; symbols λ' and λ'' will be used as the antilogs of λ and 2λ. Thus, in the above example of $\lambda = 0{\cdot}50$ and $2\lambda = 1{\cdot}00$, we have $\lambda' = 3{\cdot}2$ and $2\lambda = 10$. Two thirds of all vanadium determinations should fall within $32 \times 3{\cdot}2$ (100 ppm) and $32 \times 1/3{\cdot}2$ (10 ppm), and 95% between 32×10 (320 ppm) and $32 \times 1/10$ (3·2 ppm). The actual nature of the distribution may therefore be regarded as of a *reciprocal* type and is visualized more easily this way than when using the transformed (log) values.

Statistical data for each element in granite and diabase are given in Table 2. Elements are arranged in order of increasing dispersion, as indicated by λ and λ'. The relative deviation (C)* is included also as its magnitude serves as an approximate and easily calculated measure of dispersion. C should never, however, be used for predictions, unless dispersion is small otherwise completely unreal (negative) and false calculations will be made. Table 2 shows quite clearly that the amount of dispersion varies very considerably, from a minimum of $\lambda = 0{\cdot}07$ ($\lambda' = 1{\cdot}17$) for gallium in granite and diabase to a maximum of $\lambda = 0{\cdot}73$ ($\lambda' = 5{\cdot}6$) for chromium in diabase.

Variation and comparison of dispersion is demonstrated most effectively with the aid of frequency distribution diagrams. Although Figs. 1 to 20 cannot be used as such because ordinates and intervals vary, they may serve as master curves for the construction of equal-interval frequency distribution curves in which the ordinate is expressed as a percent; these are shown in Fig. 21.

* Based on assumed normal distribution. % Standard deviation, coefficient of variation and percent spread are synonymous.

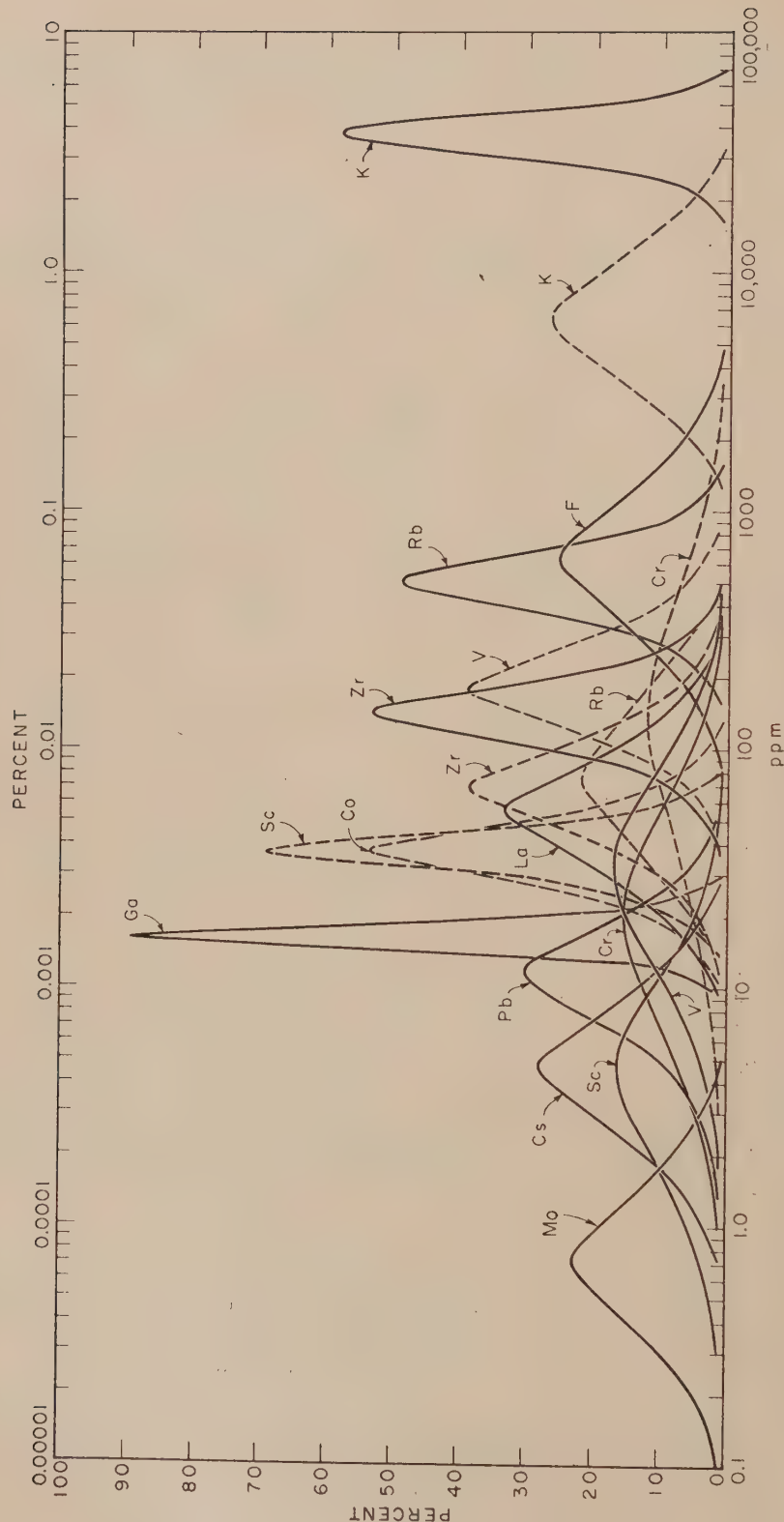

Fig. 21. Equal-interval frequency distribution plots for each element in granite (———) and diabase (— — —). Five intervals per cycle, as given by power factor of 1·58.

A log scale has been chosen as abscissa because this facilitates inspection of the curves. The common interval is given by a power factor of 1·58. This is a convenient factor as $1{\cdot}58^5 = 10$ and hence each cycle contains exactly 5 intervals, namely (starting with say 10 ppm),

		(*log value*)
$10^{1{\cdot}58} =$	15·8	1·20
$15{\cdot}8^{1{\cdot}58} =$	25·0	1·40
$25{\cdot}0^{1{\cdot}58} =$	40·0	1·60
$40{\cdot}0^{1{\cdot}58} =$	63·0	1·80
$63{\cdot}0^{1{\cdot}58} =$	100·0	2·00

All curves should be of about equal area and this is approximately the case.

Widths of the equal-interval curves should and do vary fairly regularly with the magnitudes of λ (or C) in Table 2. Irregularities are apparent but closer accordance between graphical presentation and calculated λ could hardly be expected from the moderate number of observations at hand. For example, Zr in diabase and La in granite have $\lambda = 2{\cdot}0$ and 1·9 respectively: although their frequency distribution curves are similar, their relationship in Fig. 21 is the reverse of that indicated by λ. These are, however, for the time being at least, minor irregularities and many more determinations would be required before full quantitative accordance could be expected.

In accordance with its value of $\lambda = 0{\cdot}73$, the distribution curve for chromium in diabase shows a greater dispersion than that of any other element so far investigated in an igneous rock. Gallium shows the minimum and its curve in Fig. 21 refers both to granite and diabase because the individual curves for each of the two rock types are indistinguishable. The observed dispersion of this element is so small in fact, that part of it (perhaps almost a half) is undoubtedly due to analytical error. The gallium distribution curve has consequently been elongated slightly so as to conform more closely with what probably is its actual dispersion. The distribution curve for potassium in granite has been compressed slightly so as to conform more closely with $\lambda = \sim 0{\cdot}13$.

The dispersion of an element in diabase may differ considerably from its dispersion in granite. Scandium is a striking example—very small in diabase and very large in granite; vanadium is similar. See also, Zr, K and Rb. Chromium has a large dispersion in both diabase and granite. Dispersion of the three geochemically associated alkali metals, K, Rb, and Cs, is of interest. Whereas K and Rb show small and similar dispersion in granite, that of Cs is considerably greater.

An Example of Lognormal Distribution in a Mineral

Ahrens and Liebenberg (1950) have determined tin in several specimens of mica, including thirty-eight of muscovite, mainly from pegmatites. The distribution plots in Fig. 22 have been prepared from their data. The linear plot shows

very decided positive skewness whereas the log plot is reasonably normal and hence distribution is lognormal (or very nearly so).

Relevant statistical data calculate as:

$$C = \sim 1000\%$$
$$\lambda = 0{\cdot}9$$
$$\lambda' = 8{\cdot}0$$
$$\text{arithmetic mean} = 500 \text{ ppm}$$
$$\text{geometric mean} = 100 \text{ ppm}$$

Dispersion is extreme.

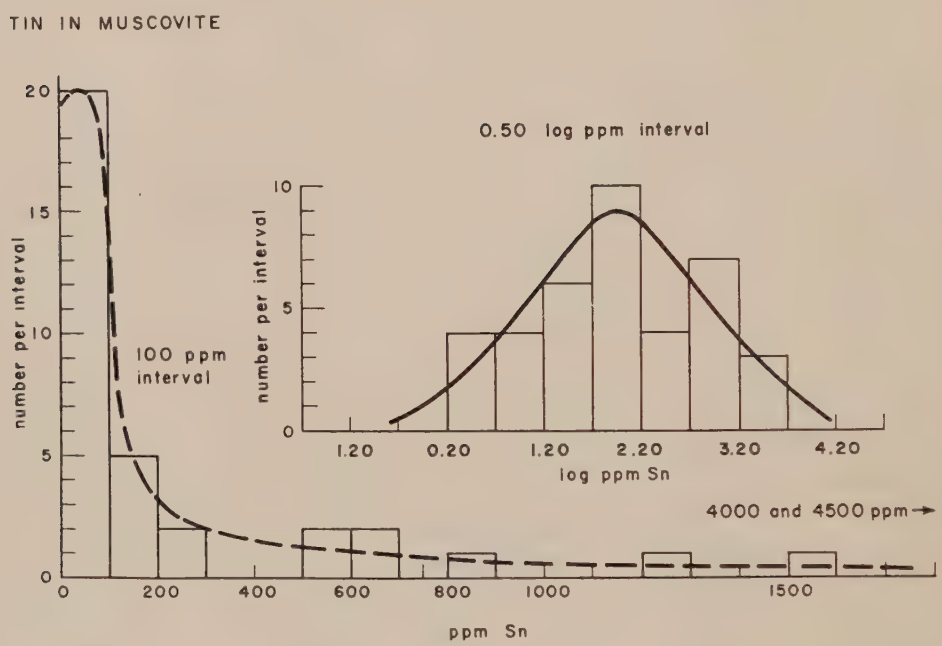

Fig. 22

Arithmetic Means (Abundances) and Geometric Means (Most Prevalent Concentrations): a Second Geochemical Law

The arithmetic mean (average) of a series of determinations gives the abundance of an element irrespective of what the nature of its distribution happens to be. If dispersion is large, however, in a lognormal distribution, the arithmetic mean becomes positively displaced with respect to the mode; this is the most frequent observation and is given by the geometric mean. One example is shown graphically in Fig. 19.

Ratios of the arithmetic mean (am) to the geometric mean (gm) have been given in Table 2 where it may be observed that they vary more or less regularly with the magnitude of λ. This relationship is shown graphically in Fig. 23 which relates am/gm to λ. am/gm remains at unity up to $\lambda = \sim 0{\cdot}1 - 0{\cdot}2$ and then

increases steeply. Chromium in diabase is not accurately located because some high chromium concentrations could not be determined accurately: the calculated value of am/gm is, however, almost certainly a minimum; hence the arrow.

The relationship between arithmetic mean and geometric mean, shown fairly

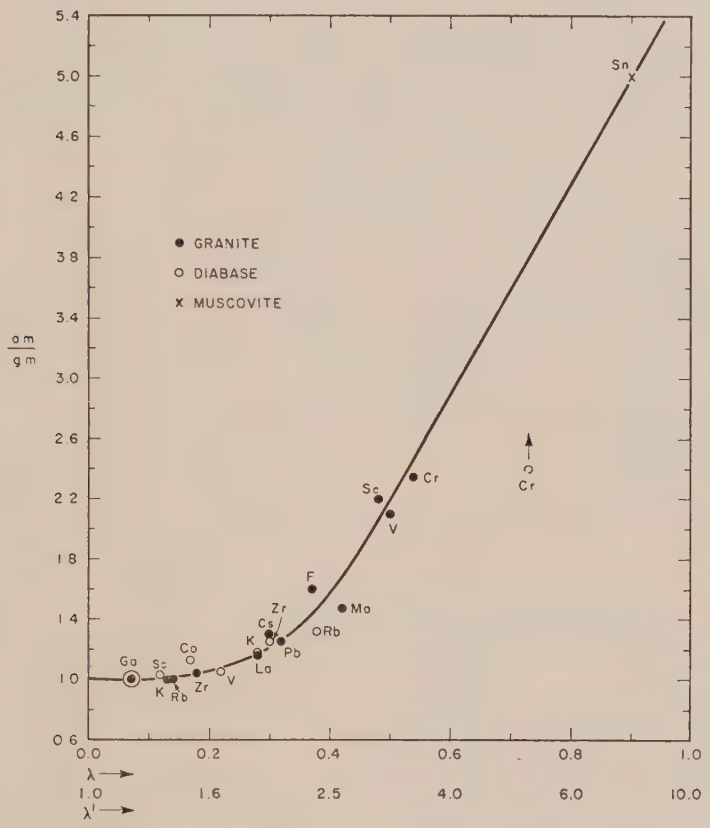

Fig. 23. Graphical presentation of the second law concerning the nature of the distribution of the concentration of an element.

quantitatively in Fig. 23, leads to the statement of a second geochemical law concerning the nature of the distribution of the concentration of an element, namely:

The abundance of an element in an igneous rock is always greater than its most prevalent concentration; the difference may be immeasurably small or very large and is determined solely by the magnitude of the dispersion of its concentration.

This law follows directly from the fundamental law and may be regarded as its subsidiary.

The largest difference between arithmetic mean and geometric mean (rocks and minerals) which has been observed so far is that of tin in muscovite where the average (500 ppm) is $\times$ 5 greater than the most common concentration (100 ppm)—see Fig. 23.

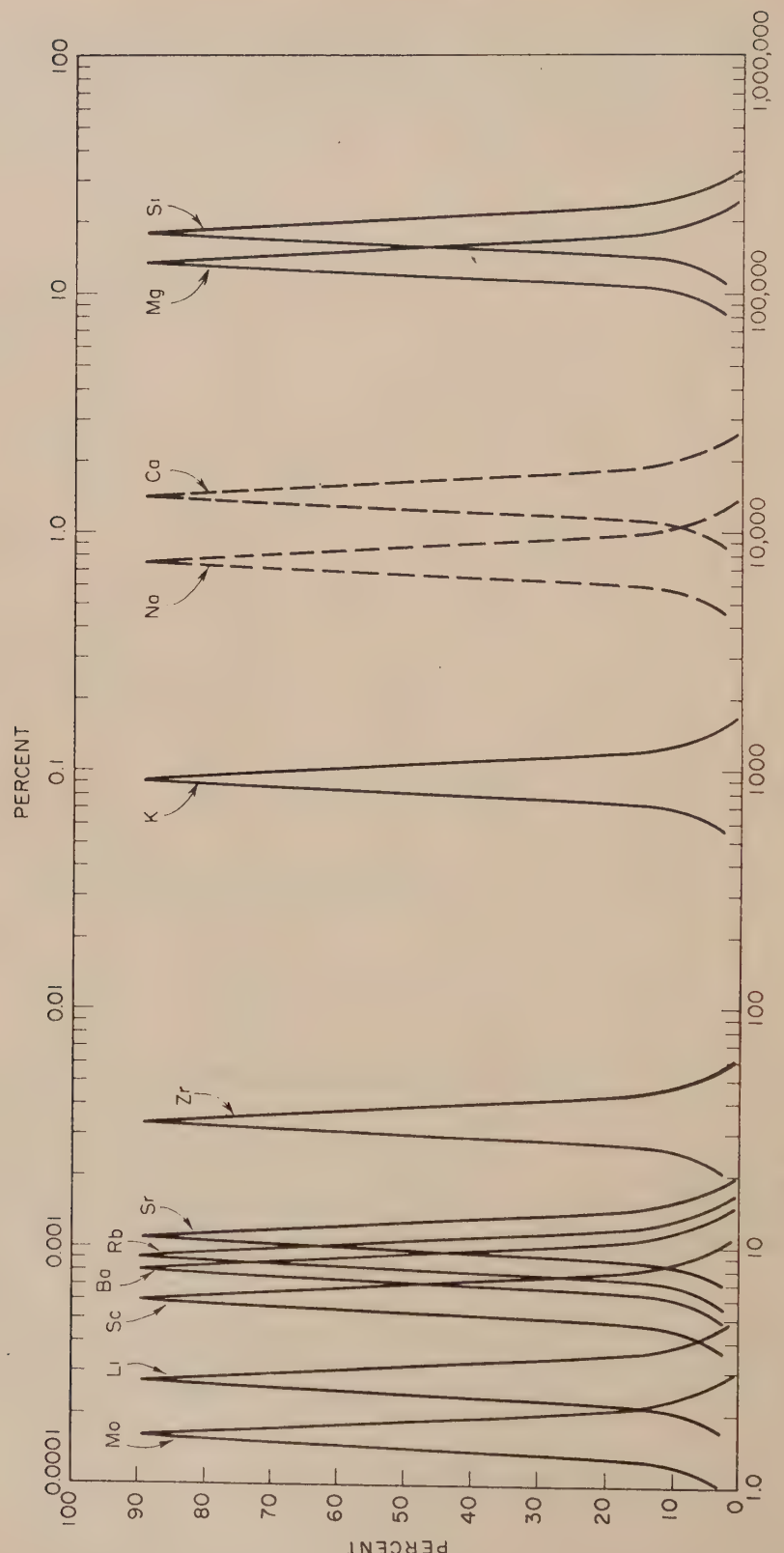

Fig. 24. Equal-interval frequency distribution plots for several elements in chondrites. (See comments in the text.)

Chromium and gallium in Canadian granite make an interesting comparison. The most prevalent concentration of each is 17 ppm, but whereas the abundance of gallium in granite is also 17 ppm, that of chromium is 40 ppm.

The Dispersion of Some Elements in Chondrites

The data in a recently published table of "superior" analyses (Urey and Craig, 1953) emphasize the fact (see Brown and Patterson, 1947, in this respect) that silicon, magnesium, total iron and to a lesser extent, Al, Ca, Na, are fairly uniformly distributed in these materials. Other elements represented in the collection of "superior" analyses show much greater variation. The author is of the opinion,

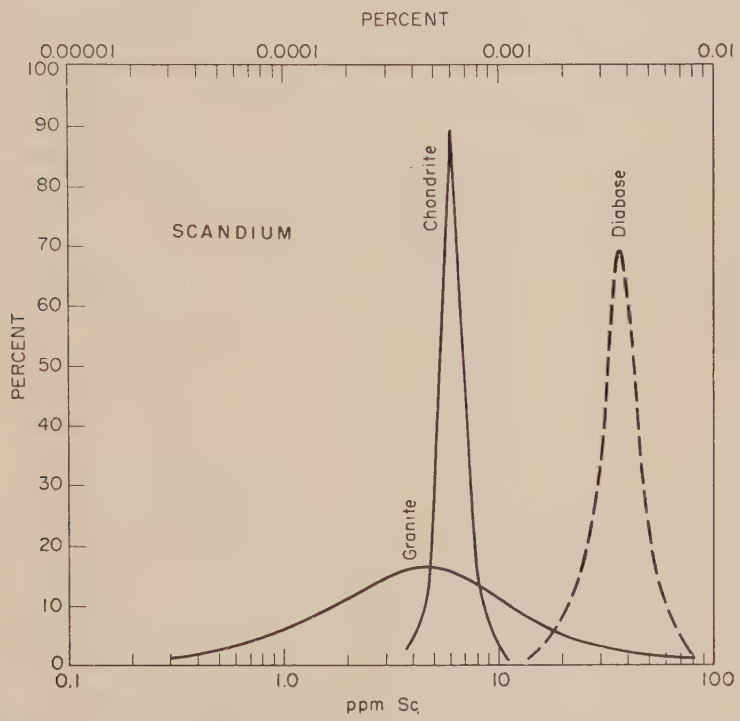

Fig. 25. Variable dispersion of scandium in granite diabase and chondrites.

however (see also Pinson, Ahrens and Franck, 1953) that the apparent greater dispersion of these elements is due mainly to analytical error and hence their determinations will not be used for the purpose of making comparisons.

Quantitative spectrochemical determinations of Li, K, Rb, Sc, Sr, Ba, and Zr (Ahrens, Pinson and Kearns, 1952; Pinson, Ahrens and Franck, 1953) show that the concentrations of these elements are also remarkably uniform in chondrites; Mo shows an equally small dispersion (Sandell, 1953). Pinson, Ahrens and Franck (1953) calculate that $C = 15$–30% for each of the elements they investigated. As the spectrochemical determinations were made with procedures which did not employ an internal standard and are therefore inferior to

those used for the rock analyses, analytical error has undoubtedly made a significant contribution to total C. Its extent is difficult to assess exactly but is likely to reduce C to $\sim$10–15%, a magnitude of dispersion equivalent to that shown by gallium in granite and diabase.

Fig. 24 shows distribution plots of some elements in chondrites, all drawn to the scale of Fig. 21 and equivalent in shape to $C = \sim$10–15% ($\lambda = \sim$0·06). The fact that each distribution curve is shown as identical should not be taken to indicate that observed dispersions are all exactly the same: dispersion is always small, so small in fact that the nature of the available data (number and accuracy of determinations) do not enable us to determine whether the small calculated variations in C are actual or not. Hence, for the time-being, curves of equal dispersion have been drawn and though not fully accurate, they can nevertheless serve to emphasize (1) that the amount of dispersion remains more or less uniform over the whole of the 100,000 fold concentration range (Si to Mo) that has been investigated, and (2) that this remarkably small dispersion contrasts quite sharply with the amount of dispersion shown by most elements in igneous rocks. (The distribution curves for sodium and calcium are not based on direct evidence but rather on the fact that their dispersion in chondrites should be very similar to potassium and strontium, respectively).

Equal-interval dispersion curves for scandium in chondrite, diabase and granite are shown in Fig. 25. This provides further emphasis of an earlier observation that one element might show totally different dispersion in different specific materials.

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Appendix

Locality details of Canadian granite referred to in Table 1

(G–1	Westerley, Rhode Island)
KB–1	Balachey Lake, Granite boulder in conglomerate above unconformity
KB–2	Balachey Lake, Granite boulder in conglomerate above unconformity
KB–3	North of Balachey Lake, from below unconformity, intruded by porphyry
KB–4	South of Balachey Pt., from below unconformity
KB–5	South shore of Handley Page Lake
KB–6	2 miles west of Tree Lake
KB–7	Southwest bay of Contact Lake
KB–8	Granite dike, South of Piy Island, Clut Lake
KB–9	Southwest shore of Cool Lake
KB–10	Granite-porphyry, Northeast shore of Sunset Lake
KB–11	Southeast shore of north arm of Conjuror Bay
KB–12	Granite on 3 islands at head of Clut Lake
KB–13	Granodiorite southwest of White Eagle Falls
KB–14	Granodiorite, east of Grovard Lake (at contact)
KB–15	Southwest of White Eagle Falls
KB–16	Granodiorite, north of Esker Lake
KB–17	Great Bear Lake
KB–18	Great Bear Lake
KB–19	Great Bear Lake
48–63	Nipissing, Askin township, west of Rankin Lake
48–115	Nipissing, Milne township, east of Tent Lake
48–158	Nipissing, Milne township, east of Tent Lake
48–188	Nipissing, Olive township, north of Mann Lake
48–407	Highway south of Martin Lake, McLaren township, Nipissing
48–411	Highway south of Martin Lake, McLaren township, Nipissing
48–421	Nipissing, Sick township, south of Martin River, Highway 11
48–422	Nipissing, Sick township, south of Martin River, Highway 11
48–472	Nipissing, Milne township, west of Florence Lake
48–476	Nipissing, Milne township, Florence Lake
48–485	Nipissing, Best township, south of Pike Lake, Highway 11
48–489	Nipissing, Cassels township, Highway 11
48–490	Nipissing, Strotty township, Highway 11, opp. mileage 77 on T. and N.D. Rly.
48–494	Nipissing, Strathecona township, near Herridge Lake
48–495	Nipissing, Olive township, south of Jumping Caribou Lake
48–496	Nipissing, Bastado township, Highway 66
48–510 → 17	Ontario, Sudbury district, composite chip sample across Creighton Granite
48–518 → 20	Nipissing, Olive township, north of Olive Lake, Highway 11
48–521, 2	Nipissing, Olive township, north of Olive Lake, Highway 11

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Recent studies on iron meteorites. V

Improved methods for the isolation of uranium and thorium from meteorites

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ABSTRACT

A method is described for the separation of 10^{-8}g quantities of thorium from solutions of iron meteorites, using 1-(o-arsono-phenyl-azo)-2-naphthol-3 : 6-disulphonic acid as a precipitant and zirconium as a carrier: uranium present has been shown to remain quantitatively in solution. Two methods are described for the recovery of uranium, in a sufficiently pure state for fluorimetry: these are solvent extraction and paper chromatography.

A ^{233}U tracer technique, combined with fluorimetry, has allowed reliable estimates to be made of meteoritic uranium.

1. Introduction

Recent studies [1] have led to the belief that the helium in iron meteorites is partly of radiogenic origin (^4He) and partly of cosmic ray origin (^3He and ^4He).

Attempts are being made to determine the contributions which these sources make to the helium in meteorites, and for this reason the uranium and thorium contents of many meteorites have been measured [2]. These elements are present in iron meteorites in about 10^{-8}g/g quantities.

In a recent description of the methods of isolation and estimation of uranium and thorium [2], there was included a procedure for their isolation from one and the same sample of meteorite. This involved the preparation of a solution of the meteorite, from which the bulk of the iron was removed by solvent extraction; there followed the co-precipitation of the uranium and thorium on added iron and aluminium carriers. These were then separated by a hydrogen peroxide-sodium hydroxide treatment. Subsequent recovery of the uranium involved the hazard of evaporating 400 ml quantities of ether containing nitric acid. The reagents involved, sodium hydroxide, hydrogen peroxide and distilled water, were also liable to contain traces of uranium and thorium. For these reasons, the use of organic precipitants, unlikely to contain any uranium or thorium, was investigated.

2. Separation of Uranium and Thorium using Organic Precipitants

The guiding principle used in the choice of organic precipitants was the following: organic reagents were chosen so that insoluble compounds were formed with a carrier element, present on a micro scale, and either uranium *or* thorium: it was a proviso of the method that the iron and other elements present in investigations of meteorite solutions, should remain in solution or not interfere, and that the carriers or reagents used should not interfere in subsequent estimations of the uranium or thorium.

In developing the methods, tracer elements were used for thorium and uranium. The tracer used for the thorium was UX_1(^{234}Th) available as chloride in dilute hydrochloric acid with 0·1 mg/ml of iron as carrier. The 2·3MeV β-particles from

the equilibrium amount of UX_2 were counted and 0·1 ml of the solution gave 130 counts per minute. ^{233}U was used as a tracer for uranium: a source from 0·1 ml of the solution of uranyl nitrate in dilute nitric acid gave 140 counts per minute in an α-particle scintillation counter.

Rao, Murthy and Rao's method [3] of using m-nitro-benzoic acid as a precipitant for milligram amounts of thorium, leaving uranium in solution, was investigated on a sub-microgram scale. The usual carriers for thorium, viz. aluminium, iron, chromium, cerium and lanthanum, would not precipitate under the required conditions: it was established however that zirconium would produce a precipitate with m-nitrobenzoic acid, without carrying uranium out of solution. Unfortunately, in adjusting the conditions to those required (pH 2·6—2·8, 80°C), if iron was present—as would be the case in meteorite estimations—it was liable to precipitate before addition of the reagent, with risk of loss of some uranium. Addition of acetic acid to avoid this loss resulted in only 50% recovery of the thorium tracer. This was probably due to complexing between the acetate and the zirconium. The method of using m-nitro-benzoic acid was therefore abandoned.

Parasonic acid [4] has been used as a precipitant for thorium and zirconium [5]. Though successful in hydrochloric acid solutions, the method was unsuccessful in dilute nitric acid: the former acid would have interfered in subsequent uranium extractions [6].

Kuznetsov [7] reports that thorium can be precipitated at pH 0·3—1·0 using 1-(o-arsono-phenyl-azo)-2-naphthol-3 : 6-disulphonic acid. This reagent was also shown to precipitate zirconium in dilute nitric acid (about 0·2N). It will be seen that the use of this reagent, and zirconium as a carrier, allowed successful separations of meteoritic thorium, leaving the uranium in solution for subsequent isolation.

Before this reagent could be used it had to be established that: (1) thorium was quantitatively precipitated with zirconium from solutions, (2) precipitation of zirconium did not remove uranium from solution.

3. Co-precipitation of Zirconium and Thorium

The following test was made on the efficiency of co-precipitation of thorium: 10 mg of zirconium as nitrate with a few milligrams of the principal elements likely to interfere in a meteorite analysis, viz. iron and chromium, were dissolved in 0·2N nitric acid. 1 ml of the UX_1 solution was added as a tracer for thorium and this was followed by a 5% by weight aqueous solution of the sodium salt of the 1-(o-arsono-phenyl-azo)-2-naphthol-3 : 6-disulphonic acid: the strawberry red precipitate which formed was centrifuged off and washed. It was then boiled with 1–2 ml of concentrated hydrochloric acid and the solution diluted to 10 ml. 1 ml portions were evaporated on to nickel trays for Geiger counting.

Thorium recoveries amounted to 98·6 $\pm$ 1·5%, 101·2 $\pm$ 1·6% and 99·3 $\pm$ 2·1%. The errors quoted here, and subsequently, refer to counting errors only.

Application to meteorite analysis

Meteorite samples were treated initially as in a previous publication, except that only aluminium was added as a carrier [2]. After the bulk of the iron had been

removed by ether extraction a few mg of aluminium were added as carrier and the uranium, thorium, aluminium, iron and any chromium present precipitated with carbonate free ammonia. A few mg of barium added prior to the precipitation retained radium isotopes in solution. The hydroxides were dissolved in nitric acid. barium "hold-back carrier" added again, and the hydroxides reprecipitated and dissolved in 0·2N nitric acid. Zirconium carrier was then added and this, together with the meteoritic thorium, precipitated with 1-(o-arsono-phenyl-azo)-2-naphthol-3 : 6-disulphonic acid. The precipitate was dissolved in 1–2 ml of concentrated hydrochloric acid and set aside for the growth to equilibrium of ThX.

ThB and ThC were then precipitated as in the previous publication and the α-activity of the ThC measured in a scintillation counter.

4. Isolation of Uranium after Precipitation of Zirconium and Thorium

Having demonstrated the quantitative co-precipitation of thorium with zirconium, experiment now showed that if uranium was present initially, it was left quantitatively in solution. Two methods are described for the recovery of the uranium.

(*a*) *Recovery of uranium by solvent extraction* [8]

This method is similar to that described in a previous publication [2]. The first tests were performed with uranium at the 10^{-5}g level. 10 mg of zirconium as nitrate and $1{\cdot}25 \times 10^{-5}$g of uranium as uranyl nitrate together with a few milligrams of the principal elements likely to interfere in a meteorite analysis, viz. iron and chromium were dissolved in 0·2N nitric acid. A 5% by weight aqueous solution of the sodium salt of the sulphonic acid reagent was added and the precipitate which formed was centrifuged off. Before fluorimetric estimation of the uranium, quenching elements were removed as follows. The solution was boiled with 20 ml concentrated nitric acid, ammonium nitrate (10 g) added as salting out agent and the solution was extracted four times with ether. The total volume used was 80 ml (compared with 400 ml in the method previously described [2]). The ether solution was shaken three times with 10 ml portions of concentrated nitric acid, saturated with ammonium nitrate, to remove traces of iron and chromium. The 30 ml of concentrated nitric acid were then extracted twice with equal volumes of ether to recover lost uranium.

The combined ether extracts were evaporated over 100 ml of water (care!) and the aqueous solution reduced to 10 ml and divided into aliquots for fluorimetry. These solutions were evaporated on platinum trays, sodium fluoride was added and fused. Fluorimetric analysis showed that in three experiments, $98{\cdot}8 \pm 2.0\%$, $99{\cdot}4 \pm 2.0\%$, $99{\cdot}2 \pm 1{\cdot}5\%$ of the uranium had been recovered. Quenching elements were absent, as was shown by "spiking" the phosphors with known weights of uranium. The errors quoted are calculated only from the spread in the fluorimeter readings for nine phosphors. Retention of uranium in solution was confirmed by dissolving the zirconium precipitate in nitric acid: portions of the solution were examined fluorimetrically and it appeared that less than 2% of the uranium had been lost.

Using ^{233}U as a tracer for uranium at the $2{\cdot}5 \times 10^{-8}$g level, 0·1 ml of the ^{233}U

solution was added before zirconium precipitation and the ^{233}U recovered in a similar manner. Recoveries from the solution after zirconium precipitation were 97·0 ± 1·4% and 100·8 ± 1·4%: the precipitate contained less than 2·5% of the available uranium.

Application to meteorites

Since it appeared that uranium was left quantitatively in solution during the precipitation described, the method was applied to the analysis of meteorite uranium: thorium was removed and estimated as in Section 3, and the uranium as in Section 4 (*a*).

(*b*) *Recovery and purification of uranium by paper chromatography*

Introduction

After the isolation of thorium from meteorite solutions, it was found that the solutions containing uranium were contaminated with iron and chromium: both elements interfere in fluorimetric estimation of uranium. It has been found that the chromium can be separated from the iron and uranium by precipitating these latter elements as ferrocyanides and that the uranium can be separated from the iron by paper chromatography, in a state sufficiently pure for fluorimetry.

The reliability of the recovery process for uranium from meteorites has been improved in the following way. After removal of thorium, a measured amount of ^{233}U was added to the solution containing the meteoritic uranium. After recovering the uranium by paper chromatography, the ^{233}U activity was measured and also the total amount of uranium present was estimated by the fluorimetric technique. The fraction of ^{233}U recovered indicated the efficiency of recovery of the meteoritic uranium and if necessary, corrections could be made to the fluorimetric results.

Development of the method: separation of chromium from iron and uranium

It has been found that uranium can be co-precipitated on ferric-ferrocyanide, leaving chromium in solution.

A solution was prepared of 5 mg of iron, 10 mg of chromium and 0·1 ml of the ^{233}U solution, in dilute hydrochloric acid. The iron, chromium and uranium were precipitated with carbonate free ammonia, the precipitate centrifuged and dissolved in 20 ml of 1 : 1 acetic acid. 5 ml of potassium ferrocyanide solution (aqueous saturated solution) were added producing a precipitate of ferric ferrocyanide. This was centrifuged for 10 minutes and a sludge made of the precipitate in water. Aliquots were spread on a 3 cm diameter platinum disc and dried under a radiant heater. The discs were heated to redness to produce a "weightless" source of about 1 mg of iron as ferric oxide. The α-activity of the sources was estimated in a scintillation counter. ^{233}U recoveries amounted to 98·2 ± 0·8% and 100·8 ± 1·6%.

Recovery of uranium from ferric ferrocyanide precipitates

The precipitates, ultimately to carry meteoritic uranium, could be decomposed and the uranium recovered as follows. The precipitate was boiled with 1–2 ml of concentrated sulphuric acid and when cool, 25 ml of concentrated hydrochloric

acid were cautiously added. The solution was diluted to 150 ml, the hydrochloric acid concentration being so adjusted as to be 2N. The iron and the uranium were then precipitated with carbonate free ammonia (^{233}U tracer experiments showed that the recovery at this stage was quantitative).

The precipitate was centrifuged off and dissolved in 3–4 ml of concentrated hydrochloric acid in a 10 ml centrifuge tube fitted with a ground glass stopper. The solution was shaken three times with 5 ml of ether equilibrated with 6·5N hydrochloric acid. The ether was removed by means of a dropping tube and finally air was blown through this tube to remove ether from the warmed aqueous phase.

Paper chromatography of Iron and Uranium

Direct fluorimetric estimation of the uranium was not possible at this stage because of quenching due to iron. Further ether extraction of iron was not possible for the extraction efficiency decreases with decreasing iron concentration [9].

It was found that solvent flow of ether over uranium and iron adsorbed on filter paper, removed the iron to a level at which no quenching occurred. This method may be contrasted with that of Lacourt [10].

Transfer of uranium and iron to filter paper strips

0·5 mg. iron, ^{233}U and natural uranium were precipitated with carbonate free ammonia, and the precipitate centrifuged and dissolved in 1 or 2 drops of dilute hydrochloric acid (recoveries of ^{233}U at this stage were usually 100%: occasionally the recovery was between 80 and 100%). The amount of iron present was sometimes inadequate for complete co-precipitation of uranium. The solution was transferred to a 25 × 2 cm strip of *Whatman's No.* 1 filter paper and the strip hung from a vessel containing ether equilibrated with 6·5N hydrochloric acid. The apparatus was covered with a bell jar and left overnight. 4 cm of the paper which had originally held the iron-uranium mixture were digested in concentrated nitric acid and the suspension diluted to 10 ml.

1 ml of the suspension was evaporated on to a platinum source disc of diameter 3 cm: the disc was warmed under a radiant heater and then placed in a platinum basin where it was warmed gently to remove carbon and produce a weightless source. The activity of the source was then determined in a scintillation counter. The other 9 ml of suspension were used to prepare sodium fluoride phosphors for the estimation of uranium.

Percentage recovery of ^{233}U after chromatography was 102·8 $\pm$ 1·1%. Recovery of uranium, measured fluorimetrically, at the 10^{-6}g level was 99·2 $\pm$ 2·9%. In subsequent experiments with ^{233}U alone, recoveries were 98·2 $\pm$ 1·7%, 96·4 $\pm$ 2·6%, 99·1 $\pm$ 2·1%.

The uranium and iron distributions on a paper strip after chromatography were investigated by cutting the strip into narrow sections and estimating their contents of the two elements. A typical result is shown in Fig. 1.

Application to meteorites

In practice in the estimation of uranium in meteorites ^{233}U was added immediately after the separation of thorium; it would have been unwise to add an α-active

tracer to meteorite solutions before removal of thorium. The α-activity of the ThC to be isolated from the thorium was of the order of one count per hour and contamination by ^{233}U might have arisen. Meteoritic uranium and ^{233}U were recovered by the procedure described and estimated by fluorimetry and scintillation counting respectively. The results from the ^{233}U estimation allowed corrections to be made to the figures for the recovery of natural uranium.

Tests on the whole procedure by adding ^{233}U after separation of zirconium gave the following percentage recoveries: $102{\cdot}4 \pm 1{\cdot}8\%$, $90{\cdot}8 \pm 2{\cdot}4\%$,

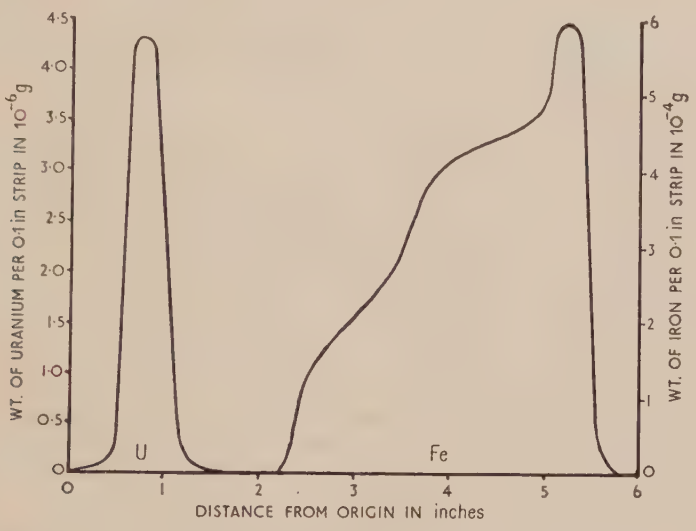

Fig. 1. Distribution, after paper chromatography, of iron and uranium placed originally between 0 and 1·6 ins.

$102{\cdot}0 \pm 2{\cdot}1\%$, $84{\cdot}5 \pm 1{\cdot}2\%$. (Low recoveries are attributed to the small amounts of iron present after the small scale ether extraction.) Recovery of added uranium ($1{\cdot}25 \times 10^{-5}$g) in a trial experiment was $100{\cdot}9 \pm 1{\cdot}8\%$.

Reagent Blanks

As the amount of tracer ^{233}U used was only $2{\cdot}68 \times 10^{-8}$g the interference with fluorimetric estimation was small. The correction to be applied was calculated from the reagent blank, which included the ^{233}U. Interference of natural uranium with the ^{233}U α-particle counting was negligible.

The thorium content of the reagents in a typical estimation involving 40 g of meteorite, was about 3×10^{-7}g of thorium: the uranium content of the reagents used was about 6×10^{-8}g.

5. Results

These methods of analysis for thorium and uranium have been applied to several meteorites. The results will appear elsewhere, in connection with the helium content and age of meteorites.

Analyses have been repeated on several meteorites already investigated [2]: the comparisons are shown in the following table.

Meteorite	Uranium in 10^{-8} g/g					Thorium in 10^{-8} g/g	
	Present Methods		Previous Methods			Present Method	Previous Method
	Solvent Extraction	Paper Chromatography	Peroxide Separation	Retrograde Extraction	Radon Thoron	Zr/organic Reagent	Peroxide Separation
Bethany Harvard	0·78 ±0·02		0·61 ±0·03			0·94 ±0·18*	2·46 ±0·58*
Carbo		0·57 ±0·03	0·52 ±0·02	0·45 ±0·03 0·56 ±0·04		0·68 ±0·19	0·63 ±0·20
Savik		0·23 ±0·02	0·18 ±0·02 0·25 ±0·02 0·23 ±0·04	0·21 ±0·03	0·20 ±0·05 0·22 ±0·05		

* Samples taken from points 2 ins. apart in an iron meteorite containing inclusions.

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A calculation of the amount of weathered igneous rock

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ABSTRACT

The quantity, 6 462 kg cm^{-2}, is calculated for the total of igneous rock weathered during the geologic history of the Earth, viz., $3{\cdot}5 \times 10^9$ years. The calculation is based on the assumptions that all ^{40}A now found in the atmosphere and the hydrosphere is a decay product of ^{40}K in the Earth's crust, and that all ^{40}A formed has been released by weathering.

Knowledge of the total amount of igneous rocks in the surface layers of the Earth that has been decomposed by weathering during the geologic history of the Earth is of importance for geochemical calculations. Goldschmidt (1933), starting from the sodium content of igneous rocks, sea water, and sediments, computed the total of weathered igneous rocks as 160 kg cm^{-2}. This calculation, however, gives only an approximate estimate and is open to various criticisms (see Rankama and Sahama, 1952, p. 223). Another calculation made by C. W. Correns (quoted in Houtermans and Jordan, 1946, p. 127) on the basis of the sodium and potassium content of igneous rocks, sea water, and sedimentary rocks gave 156 kg cm^{-2} as the total of weathered igneous rock.

The quantity of weathered igneous rock, however, may be calculated by a method based on the radioactive decay of the potassium isotope, ^{40}K. This nuclide decays dually, producing stable ^{40}Ca by negative beta-emission and stable ^{40}A by K-capture to an excited state of ^{40}A, followed by gamma-ray emission to its ground state. The branching ratio, λ_K/λ_β, of the decay is 0·126 (Inghram and others, 1950). Therefore, 88·8% of ^{40}K decay by beta-emission and 11·2% decay by K-capture. The disintegration constant for beta-decay is $\lambda_\beta = 1{\cdot}54 \times 10^{-17}$ sec^{-1} (Morrison, 1951), or $4{\cdot}85 \times 10^{-10}$ year^{-1}. Calculation of the disintegration constant for K-capture from λ_β and λ_K/λ_β gives $\lambda_K = 0{\cdot}61 \times 10^{-10}$ year^{-1}. Consequently, the total decay constant is $\lambda = \lambda_\beta + \lambda_K = 5{\cdot}46 \times 10^{-10}$ year^{-1} that, inserted in the equation, $T = ln\ 2/\lambda$, gives for the half-life of the decay the value $T = 1{\cdot}27 \times 10^9$ years. The observed half-life is $1{\cdot}33 \times 10^9$ years (Houtermans, Haxel, and Heintze, 1950; Gráf, 1951). These nuclear data serve as a basis for the calculation to be presented in the following paragraphs.

The abnormally high terrestrial abundance of ^{40}A (99·600% in atmospheric argon; Nier, 1950, p. 792) was first suggested by v. Weizsäcker (1937) to be a result of the production of ^{40}A in the decay of ^{40}K. The available evidence indicates that the primordial terrestrial atmosphere, including the bulk of the inert gases, was lost nearly entirely in a very early stage in the Earth's evolution (Brown, 1949, 1952; Suess, 1949). Consequently, one must assume that radiogenic ^{40}A (^{40r}A) released by rock weathering and in volcanic gases has accumulated in the atmosphere in the course of geologic time. Much ^{40r}A, moreover, is dissolved in the hydrosphere. Some of it is the decay product of ^{40}K contained in sea water.

The amount of igneous rock required to produce the ^{40}A now present in the atmosphere and the hydrosphere may be calculated as follows.

The total quantity of argon in the atmosphere is $0{\cdot}655 \times 10^{20}$ g (Rankama

and SAHAMA, 1952, p. 305) of which 99·6%, or 0·652 × 10^{20} g, consist of ^{40}A. The content of dissolved "argon" (residue after the extraction of nitrogen) in sea water varies between 0·2 ml l^{-1} and 0·4 ml l^{-1} (SVERDRUP, JOHNSON, and FLEMING, 1946, pp. 187, 189); the average for the argon content used in this calculation is 0·3 ml l^{-1}, or 0·52 × 10^{-6} g g^{-1}. From the total mass of the ocean of 14 060 × 10^{20} g (RANKAMA and SAHAMA, 1952, p. 264) and the argon content the total quantity of dissolved argon in the ocean water is calculated as 7 311·2 × 10^{14} g, and the proportion of ^{40}A of the total is 7 282 × 10^{14} g. According to GOLDSCHMIDT (1933), there are 0·1 kg fresh water and 278·11 kg sea water for every cm^2 of the Earth's surface. Assuming that the content of dissolved argon in fresh water is as high as its content in sea water, one obtains 2·6 × 10^{14} g for the total amount of argon dissolved in fresh surface water and, likewise, 2·6 × 10^{14} g for the total of dissolved ^{40}A. The amount of argon adsorbed in snow and soil is negligible (see SUESS, 1949, p. 602). Consequently, the grand total of ^{40}A present in the hydrosphere and the atmosphere is approximately 659 285 × 10^{14} g.

The average potassium content of igneous rocks in the surface part of the lithosphere accessible to observation is 25 900 g ton^{-1} (RANKAMA and SAHAMA, 1952, p. 39), and the contribution of ^{40}K with a relative abundance of 0·119% (NIER, 1950, p. 793) is 3·1 g ton^{-1}. The revised age of the Earth's crust, according to COLLINS, RUSSELL, and FARQUHAR (1953), is 3·5 × 10^9 years*. At a time 3·5 × 10^9 years ago, the amount of ^{40}K present in the average igneous rock was 6·75 times as high as today, as is calculated from the equation, $\log N_0 = 0{\cdot}30103\ t/T$, where N_0 is the number (and, for the decay of ^{40}K, also the mass) of atoms of a radionuclide that exist at a time, t, and T is the half-life of the radionuclide (for ^{40}K, 1·27 × 10^9 years). Consequently, the original ^{40}K content of igneous rocks of the upper lithosphere was 20·9 g ton^{-1}. The difference, or 17·8 g ton^{-1}, has decayed to produce, in accordance with the branching ratio, 2·0 g ton^{-1} ^{40r}A and 15·8 g ton^{-1} ^{40r}Ca. In other words, an average of 10^6 g of igneous rock was required to produce 2·0 g ^{40r}A. The amount of igneous rock required to produce the total quantity of ^{40r}A now present in the atmosphere and the hydrosphere, viz., 659 285 × 10^{14} g, is calculated as 329 643 × 10^{20} g. Divided by the total surface area of the Earth, viz. 5·101 × 10^{-18} cm^2 (BIRCH, SCHAIRER, and SPICER, 1942), this gives 6 462 kg cm^{-2} as the total quantity of the ^{40r}A-producing igneous rock. This value is approximately 40 times as high as GOLDSCHMIDT's estimate of the total of weathered igneous rock. Computation of the thickness of the layer of a chemically homogeneous crust of "average" igneous rock that corresponds to the 329 643 × 10^{20} g of igneous rock gives a result of 22 km. Consequently, provided all argon formed in the rocks has been released into the atmosphere, it appears that all the ^{40}A now present in the geospheres beyond the lithosphere was produced in the crustal layers of the Earth.

This result is at variance with the conclusion of KULP (1951) that there is far too much ^{40}A in the atmosphere to have derived only from crustal rocks. KULP

* PATTERSON, TILTON, and INGHRAM (1953), on the basis of uranium and lead-isotope abundance measurements in the Earth's crust and in meteorites, found an age of approximately 4·6 × 10^9 years for the Earth. In view of this new evidence, perhaps it is not too bold to assume that the "age of the crust" of 3·5 × 10^9 years indicates the length of time during which exogenic agents have operated on the Earth's surface, i.e., the length of the real *geologic* history of the Earth.

believed that most of the atmospheric ^{40}A came from subcrustal regions and that during the past $3{\cdot}3 \times 10^9$ years only 14% of the ^{40r}A formed has leached out of the rocks. Birch (1951) made a similar calculation and found that the amount of present-day atmospheric ^{40}A is more than two-thirds of all the ^{40}A generated in a 33 km thick crust during $3{\cdot}3 \times 10^9$ years, viz., $0{\cdot}9 \times 10^{20}$ g, and that an additional amount of $1{\cdot}0 \times 10^{20}$ g was generated in a mantle of dunitic composition. He also supposed that almost all argon from the crust and a considerable fraction of argon from the mantle were released into the atmosphere. The results of Kulp and Birch, however, are affected by the new information about the potassium content of the mantle (Ahrens, Pinson, and Kearns, 1952; Holyk and Ahrens, 1953).

According to Urey (1951, p. 247), the present-day amount of ^{40}A in the atmosphere is less than 20% of the amount that has been produced in the decay of ^{40}K during the past 3×10^9 years. Only $2{\cdot}5 \times 10^8$ years would be required to produce all this argon if it were produced 3×10^9 years ago, because of the greater abundance of ^{40}K at that time. Urey concluded that at least a part of the argon might have been supplied to the atmosphere during the formation or the early history if the Earth, while the rest was supplied by degassing and other processes.

The average content of argon and of ^{40}A in igneous rocks is $0{\cdot}04$ g ton^{-1} (Rankama and Sahama, 1952, p. 39). Consequently, if $329\,643 \times 10^{20}$ g igneous rock may be expected to succumb to weathering during the next three or four billion years to come they would supply a total of $13\,186 \times 10^{14}$ g ^{40r}A into the atmosphere and the hydrosphere provided all their argon would become liberated. This quantity is only approximately one-fiftieth of the quantity of ^{40}A now present in the said geospheres, but it will be augmented by much of the ^{40r}A to be produced by the decay of ^{40}K.

Along with the argon liberated in rock weathering, much argon is released into the atmosphere by volcanic emanations. Boato, Careri, and Santangelo (1952) found that ^{40}A, evidently formed in potassium minerals, is commonly strongly concentrated in argon in boriferous volcanic emanations and in fumarole gases in Italy. The volcanic gases from Etna, Stromboli, and Vulcano indicated no essential enrichment of ^{40}A, and consequently the samples analyzed probably were air circulating in the volcanic vents. The boriferous volcanic gases at Larderello, Italy, on the other hand, were found to supply approximately $4{\cdot}4 \times 10^6$ g ^{40}A annually. This instance of the still intense degassing of the Earth also indicates that the computed amount of 6 462 kg cm^{-2} of weathered igneous rock represents a maximum. The value should be further decreased because ^{40}A is also produced by the weathering of sedimentary and metamorphic rocks ultimately formed from igneous rocks. Unfortunately, the amount to be subtracted cannot be estimated.

Because the weathering of igneous rocks does not result in a complete disintegration of all the potassium-bearing minerals, it appears that the ^{40r}A formed is not quantitatively released in weathering. Consequently, the release into the atmosphere of ^{40r}A involves difficulties, and the quantitative aspects of the history of atmospheric ^{40}A are beset with some uncertain factors, including the possible geochemical differentiation of the uppermost lithosphere (Rankama, 1946), by which potassium would tend to become continuously concentrated in the Earth's uppermost crust throughout its evolution. In any case, the amount of weathered

igneous rock calculated in this paper is sufficiently different from GOLDSCHMIDT'S value to indicate that his value can only represent a minimum.

The value calculated in this paper agrees, in the order of magnitude, with the result obtained by HOUTERMANS, HAXEL, and HEINTZE (1950, p. 666). Using a half-life of $1{\cdot}33 \times 10^9$ years for ^{40}K and a branching ratio of 0·111, they found 8 200 kg cm^{-2} as the amount of igneous rock that has produced all present-day atmospheric ^{40}A during the past 3×10^9 years. Unfortunately, they did not report the details of their calculation.

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Iron and titanium oxides in soil clays and silts

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ABSTRACT

The methods of extraction of free sesquioxides in soils are discussed. Using aluminium foil and ammonium tartrate, the readily soluble sesquioxides are removed from soil profiles and the resultant mechanical analyses are compared. Differences between iron oxide content and titanium oxide content of treated and untreated silt and clay fractions, show that there is more readily soluble material in the surface horizons and this is related to the power of humus to render soluble these relatively insoluble materials. High iron oxide content and titanium oxide content of deep horizons are believed to be due to leaching of parent rock, with consequent removal of alkalis and subsequent elevation of the sesquioxide percentage. The processes of translocation of iron and titanium are discussed.

Introduction

During the course of a systematic examination of the mineralogical constituents of some New Zealand soil profiles, an investigation was made into the degree of free oxide cementation, with particular reference to iron and titanium, in the various soil horizons. The soils investigated were derived in great part from an arkose of Mesozoic age, and to some small extent from wind-blown volcanic dust. This arkose is remarkably uniform in composition, and although the soil profiles are from widely separated regions, their parent material is constant in composition.

In hand specimens the rocks range from ashen grey to dark grey in colour, and in some cases fragments of comminuted plant detritus can be observed. Sometimes the rocks are seamed with small quartz veinlets, but these never attain large dimensions. The minerals composing the rock consist almost entirely of quartz, sodic plagioclase, some minor orthoclase and rare microcline. Antiperthitic intergrowths are often encountered, and it seems that the plagioclase may originally have carried a higher proportion of the anorthite molecule, for clinozoisite is normally present inside the crystals, often lying parallel to the cleavages.

The only primary ferromagnesian mineral is biotite, always baueritized and often chloritized. Accessory minerals are zircon, sphene, iron-ore and occasional well-rounded garnets. The iron-ore is titaniferous in nature, for it is often associated with small veins of leucoxene and dusty sphene. The ground-mass is very fine-grained and sometimes iron-stained. It appears to be micaceous in nature, and is believed to represent the sericitic product of feldspar decomposition.

Profile Descriptions

The exact localities and descriptions of the soil profiles investigated are as follows:

Profile I

Locality—North Auckland Opuawhanga Survey District 1½ miles north of Tutukaka, on the Tutukaka-Matapouri Bay Road.

Height above Sea Level—250 ft.

Slope—16° to 18°.

Vegetation—Formerly *Beilschmiedia taraire*, *Vitex lucens*, etc., of the broadleaf podocarp series. Now in paspalum and some bracken fern. (*Pteridium sp.*)

Differentiation—immature.
0 in. to 2 in. Darkish brown crumbly clay loam.
8 in. to 12 in. Yellow-brown moderately compact clay loam to clay.
20 in. to 26 in. Bright yellow-brown crumbly clay loam. Moderately compacted.
5 ft 6 in. to 6 ft Pinkish red clay loam matrix surrounding well decomposed arkosic fragments.
13 ft to 13 ft 6 in. Pinkish red decomposed arkosic material.
16 ft Arkosic parent material.
Profile 2
Locality—Canterbury Province; Hanmer—50 yds up Jolly's pass road from the forestry observation point junction.
Height above Sea Level—1,940 ft.
Slope—27°.
Vegetation—*Leptospernum scoparium*, mountain flax, and much silver tussock, moss and yorkshire fog.
Differentiation—immature.
0 in. to 1½ in. Brown loam with much admixture of grass roots.
2 in. to 11 in. Brown silt loam.
11 in. to 15 in. Yellow-brown loam.
16 in. to 21 in. Dull yellowish silt loam.
28 in. to 32 in. Yellow-brown sandy silt loam.
36 in. Arkosic parent material showing no decomposition.
Profile 3
Locality—Canterbury Province, 75 yds on the Canterbury side of the summit of the Lewis pass road.
Height above Sea Level—2,820 ft.
Slope—30°.
Vegetation—Beech forest (*Nothofagus Sp.*).
Differentiation—strongly podzolised.
0 in. to 1 in. Forest litter.
1 in. to 4 in. Dark black, peaty, humus horizon.
5 in. to 7 in. Ashen to buff grey sandy loam.
10 in. to 15 in. Dull yellow-grey sandy loam.
30 in. Ashen grey gravelly material.
36 in. Arkosic rock.
Profile 4
Locality—Otago Province, Balclutha—Owaka area. Sheet 179, 1 mile inch, 479 × 041.
Height above Sea Level—60 ft to 70 ft.
Slope—5° to 10°.
Vegetation—Forest cleared 20 years previously and now in grass. Cocksfoot, yorkshire fog, vernal and browntop association.
Differentiation—immature.
0 in. to 4 in. Chocolate-brown free silt loam.
5 in. to 8 in. Yellow-brown silt loam.
11 in. to 16 in. Dull yellow-brown loam.
28 in. to 33 in. Light yellow loam.
48 in. Arkosic Rock.
Profile 5
Locality—Wellington Province, Akatarawa Survey District. Section 3981 block 6. Summit of road to left after turn off to Akatarawa-Waikanae Road.
Height above Sea Level—1,400 ft.
Slope—16° to 18°.
Vegetation—Forest very recently cleared—*Weinmannia racemosa* and *Dacrydium cupressinum*. Now in pasture.
Differentiation—strongly podzolised.
0 in. to 6 in. Dark black silt loam, with decomposing roots.

6 in. to 8 in. Black to buff grey heavy silt loam.
8 in. to 12 in. Black to brown silt loam.
12 in. ± ½ in. Iron pan.
12 in. to 16 in. Brownish-yellow loam.
24 in. to 26 in. Powdery yellow silt loam.
40 in. to 44 in. Powdery yellow silt loam.
54 in. Weathered arkosic rock.

Methods used in Sesquioxide Extraction

Various methods have been described by different workers for the removal of the so-called "free sesquioxides." These methods grade from the use of comparatively weak solvents which have little effect on other minerals (Tamm, 1922; Jung, 1934; Robinson and Holmes, 1925; MacCarthy, 1925; Mattson, 1928, 1931) through reagents which have a greater effect (Dion, 1944; Drosdoff and Truog, 1935, 1941; Jeffries, 1941; Allison and Scarseth, 1942) to methods which severely attack iron-bearing minerals (Jeffries, 1946; Beck, 1939; Galabutskaya and Govorova, 1934). Comparisons of the various experimental procedures have been numerous (Barbier, 1936; Brioux and Jouis, 1936; Dion, 1944; Betremieux, 1949; Williams, 1950; Deb, 1950) to mention but a few. It seems generally agreed that the most efficient methods of iron removal also cause serious decomposition of other minerals and it was for this reason that an intermediate method was selected, for material subsequent to iron removal was required for other experimental work.

Method used

Two samples of ten grams of air-dried soil were treated with 10% hydrogen peroxide to destroy organic matter. One sample was transferred to an aluminium dish, boiled for one hour with 10% ammonium tartrate and then filtered and washed. Following Dion (1944) small spirals of aluminium foil were used to increase the surface available for nascent hydrogen liberation. The mechanism of the reaction is that the nascent hydrogen produced by the reaction with the aluminium cylinder reduces ferric iron to the ferrous state, and this is then in a condition to be taken into solution as a complex tartrate ion. Ammonia is liberated and escapes as gas, thus keeping the *p*H constant at 6·4 (Dion, 1944). By this means any iron oxides held by the soil as fairly free binding media were removed.

The position of titania during this treatment is not so clear, and very little work has been undertaken in the past with specific reference to "free" titania. Experiments were made with the three finely ground crystalline modifications of titanium dioxide, namely, anatase, brookite and rutile. Even continuous treatment for twelve hours with ammonium tartrate and aluminium would not dissolve the slightest trace of titanium nor would the method of Galabatskaya and Govorova (1934). On the other hand, experiments with freshly precipitated titanium dioxide showed that the method dissolved titanium in appreciable quantities. After ignition this precipitated dioxide lost its power of solubility. It has been known for some considerable time that titanium dioxide when freshly precipitated consists of hydrated titanium dioxide (Mellor, 1927)—tetrahydroxide

$Ti(OH)_4$ (sometimes called orthotitanic acid) at low temperatures, while $TiO(OH)_2$ (metatitanic acid) predominates at high temperatures. These are converted to the dioxide by ageing or strong heating. These hydrated compounds are amphoteric, and will dissolve in acids to give titanic compounds, and in alkalis to produce the titanates. It seems that the mechanism functioning in the soils investigated,

Table 1. *Mechanical analyses of untreated and treated soils*

Untreated			*Sample, and Depth in inches*	*Treated*		
Sand %	*Silt %*	*Clay %*		*Sand %*	*Silt %*	*Clay %*
			Profile 1			
14·7	33·2	42·3	0–2	10·8	20·3	54·6
10·8	28·4	57·3	8–12	10·2	20·6	63·4
9·6	22·3	65·1	20–26	9·7	18·9	65·9
22·8	26·9	46·8	66–72	23·2	27·0	47·9
45·9	29·9	22·6	156–162	55·7	24·1	22·8
			Profile 2			
38·8	23·7	26·7	0–1½	43·0	22·1	14·4
45·7	30·8	19·3	2–11	45·6	27·6	20·6
49·7	28·2	20·0	11–15	50·8	28·1	18·2
46·7	31·1	20·8	16–21	45·9	28·6	23·0
50·9	27·6	21·9	28–32	52·2	28·2	19·5
			Profile 3			
1·3	5·9	17·5	0–1	2·4	7·2	5·2
11·5	7·1	11·7	1–4	11·2	8·3	4·3
58·7	26·4	12·8	5–7	59·8	25·0	10·7
51·3	25·0	18·3	10–15	42·0	20·6	23·5
75·2	15·9	8·9	30–32	76·2	14·5	7·7
			Profile 4			
51·1	28·2	13·1	0–4	45·5	23·7	17·1
49·7	27·9	19·6	5–8	47·3	21·5	22·4
57·2	29·8	14·0	11–16	54·1	20·9	19·0
63·5	21·8	13·8	28–33	63·3	18·7	14·3
			Profile 5			
25·9	21·9	5·5	0–6	29·6	20·0	5·0
36·3	20·2	5·0	6–8	38·7	28·4	6·4
35·0	32·8	7·0	8–12	31·1	33·4	12·7
42·1	36·1	8·7	12–16	31·7	27·5	24·3
48·0	27·4	8·1	24–26	41·2	27·0	18·3
53·7	35·1	5·6	40–44	47·0	38·2	8·2

has been a solution via a preliminary hydration, followed by a subsequent precipitation. A somewhat similar process was suggested for laterites by Frederickson (1948). If this had not been the case, it seems difficult to arrive at any explanation of the titanium rendered soluble by the nascent hydrogen method, for it has been shown by experiment that the crystalline modifications of titanium dioxide are insoluble under this treatment. That the titaniferous content of the specimens is present as dioxide, is demonstrated for some specimens by faint anatase lines in the x-ray powder photographs.

After this treatment the samples were filtered and washed with water.

Both the treated and untreated samples were then made up to 250 cc. and shaken in a reciprocating shaker for twenty-four hours using ammonium hydroxide as a dispersing agent (15 c.c. of conc. NH_4OH).

The shaking concluded, the samples were made up to 500 c.c. and mechanical analyses following the international method (Robinson, 1930) were completed.

The results are shown in Table 1, where they have been arranged in an order corresponding to a gradual decrease in annual temperature. Thus Profile 1 has developed under much warmer conditions than Profile 2, etc.

Discussion

In Table 1, it should be noted that the top horizons of the podzols (Profiles 3 and 5) are extremely humus-rich, and even 100 vol. hydrogen peroxide would not remove all the organic matter. The organic material, in consequence, appears in the various fractions. Thus any comparison in the surface horizons of these soils is masked by the fact that the chemical treatment for the removal of free oxides also affects the humus, and a sudden drop in percentage clay occurs (e.g. Profile 3) owing to the more efficient removal of organic matter. It should further be noted that this chemical treatment also removes small quantities of silica and alumina and hence differences of less than $\pm 1\%$ have no significance with regard to the clay fraction.

The feature which emerges from Table 1 is that in the lower horizons, differences between treated and untreated samples are at a minimum, and in such samples percentages of clay are almost identical.

It is the percentage clay fraction which best registers any cementation effect, and clay and silt fractions from Profile 1 and clay fractions of Profile 4 were chemically analyzed. The results are shown in Table 2, where they are expressed on an ignited basis, thus eliminating any discrepancies caused by variable water and organic matter content. The treatment obviously does not remove all the iron and titanium in either the silt or the clay fractions, and the iron and titanium remaining must be much more tightly held. A comparison of corresponding silt and clay fraction analyses of Profile 1 demonstrates the rise in iron and titanium content with decreasing grain size, an effect observed and recorded by numerous workers—Robinson, Steinkoenig and Fry (1917), Steinkoenig (1914), Geilman (1920), Robinson and Holmes (1925), Joffe and Pugh (1934), but exceptions to the rule have also been recorded (Morosov, 1940).

In both the silt and the clay fractions examined, there is a steady increase in the percentage iron and titanium as the profile depth increases. The decrease in

Table 2. Iron and titanium content of clays and silts

	Profile 1													*Profile* 4						
	Silt Fraction						*Clay Fraction*							*Clay Fraction*						
	Fe_2O_3 %				TiO_2 %			Fe_2O_3 %				TiO_2 %			Fe_2O_3 %				TiO_2 %		
Depth in inches	*Untreated*	*Treated*	*Difference*	*Untreated*	*Treated*	*Difference*	*Depth in inches*	*Untreated*	*Treated*	*Difference*	*Untreated*	*Treated*	*Difference*	*Depth in inches*	*Untreated*	*Treated*	*Difference*	*Untreated*	*Treated*	*Difference*
0–2	6·40	6·28	0·12	0·73	0·62	0·11	0–2	11·44	9·86	1·58	1·96	1·77	0·19	0–4	12·20	8·13	4·07	1·70	1·45	0·25
8–12	4·79	4·74	0·05	0·78	0·57	0·21	8–12	12·68	11·78	0·90	1·57	1·47	0·10	5–8	13·89	11·22	2·67	2·19	1·90	0·29
20–26	6·02	5·59	0·43	0·78	0·65	0·13	20–26	14·68	13·73	0·95	1·76	1·70	0·06	11–16	14·19	13·65	0·54	1·94	1·94	0·00
66–72	9·48	9·41	0·07	1·25	1·18	0·07	66–72	15·17	14·72	0·45	1·69	1·67	0·02	28–33	14·82	13·92	0·80	2·12	2·12	0·00
156–162	10·25	10·03	0·22	1·52	1·53	0·01	156–162	13·46	13·35	0·11	1·80	1·76	0·04							

percentage of iron in the deepest horizon of Profile 1 is due to insufficient weathering for a greater amount of unleached material exists in this horizon, for example there is a greater amount of unweathered feldspar. Despite this general increase with depth of iron and titanium, the quantity removable by the DION method (1944) decreases with increasing depth. Other workers have noted similar effects, for instance ROBINSON and HOLMES (1925), DROSDOFF and TRUOG (1935), HOON (1936), MOROSOV (1940), MUIR (1935), but the reverse has also been recorded by COLEMAN and JACKSON (1945) and by JOFFE and KUNIN (1942).

If the higher iron and titanium content with depth were due to transport from above, it would seem reasonable to assume that such elements would be fairly easily removable. The figures demonstrate that at depth scarcely any iron and titanium is removed by the treatment. Furthermore, if the greater iron and titanium content came from above, such an origin should cause an aggregation of fine particles due to oxide films, thus the iron content of silt fractions should be considerably greater than that of the clays, and the treated and untreated silt fractions should have differing amounts of sesquioxides. The opposite is the case. It has been observed in various parts of the earth that weathered rocks invariably contain a sesquioxide percentage higher than that of the parent material (NIGGLI, 1926), and this process is believed to cause the high iron and titanium content of the deep horizons of these soils from New Zealand.

The problem of solution of iron oxide in nature has long received attention and amongst those who have studied the problem are HESTER and SHELTON (1927), OLSON (1947), BLOOMFIELD (1953), and GLENTWORTH and DION (1949).

A combination of the data of Tables 1 and 2 reveals some extremely interesting points. For convenience, Table 3 has been constructed, and in this, comparison is made between percentage clay and iron oxide contents of such samples as were chemically analyzed. It will be observed that with a rise in percentage

Table 3. *Comparison of clay and iron oxide contents*

Profile 1							*Profile* 4						
	Fe_2O_3 %		Clay %					Fe_2O_3 %		Clay %			
	1	2	3	4	1–2	4–3		1	2	3	4	1–2	4–3
Depth in inches	*Untreated*	*Treated*	*Untreated*	*Treated*	*Difference*	*Difference*	*Depth in inches*	*Untreated*	*Treated*	*Untreated*	*Treated*	*Difference*	*Difference*
0–2	11·44	9·86	42·3	54·6	1·58	12·3	0–4	12·20	8·13	13·1	17·1	4·07	4·0
8–12	12·68	11·78	57·3	63·4	0·90	6·1	5–8	13·89	11·12	19·6	22·4	2·67	2·8
20–26	14·68	13·73	65·1	65·9	0·95	0·8	11–16	14·19	13·65	14·0	19·0	0·54	5·0
66–72	15·17	14·72	46·8	47·9	0·45	1·1	28–33	14·82	13·92	13·8	14·3	0·80	0·5
156–162	13·46	13·35	22·6	22·8	0·11	0·2							

iron oxide extracted by the Dion method there is a sympathetic rise in percentage clay or silt in the treated sample. In all cases the greatest differences are to be found in the top horizons, and these horizons are the humus-rich areas.

The relationship between aggregation in soils and free oxide content has been investigated by various workers. Lutz (1936) using Drosdoff and Truog's method of extraction, was able to show a fairly direct graphical relationship between percentage aggregates and free iron oxide. Dion (1944) demonstrated that after free iron removal by his nascent hydrogen method, an increase occurred in the percentage clay. It is interesting to note that the sample in which he observed the greatest variation was from an A horizon.

Origin and Translocation of the Iron and Titanium Oxides

(1) *Iron*

The iron content of the parent rock is contained largely in the titaniferous iron ore, which is a fairly abundant accessory constituent of the arkose. The other large source is the biotite. During weathering processes the alkalis and alkaline earths are leached from the rock, and the iron content of the clinozoisite is also probably left as iron oxide. Thus the mineral grains receive a coating of iron oxide. The iron oxide is always largely amorphous in the samples studied, for x-ray diffraction photographs showed no lines which could be attributed with any certainty to a crystalline iron oxide. There were some faint lines in the powder photographs of clay fractions of deep horizons of Profile 1, which could possibly be attributed to haematite, but the evidence is not conclusive, although other workers have recorded this mineral in soils (e.g. Alexander, Hendricks and Nelson, 1939; Nagelschmidt, 1939; Fujimoto, Sherman and Chang, 1948). Although differential thermal analysis of separated fractions of treated and untreated clay fractions did not give any conclusive evidence as to the nature of the iron oxide present, there is evidently a greater tendency for crystallinity to occur with warmer conditions, and an amorphous nature with cooler conditions, for only those profiles from warmer climatic localities showed iron with any tendency towards crystallinity as adjudged from x-ray powder photographs.

The movement of iron oxide in soil has long attracted attention and various workers have conducted experiments testing the efficacy of humus, solutions from fresh and decaying plants, and various acids as solvents (Gruner, 1922; Starkey and Halvorson, 1927a, 1927b; Harrar, 1929; Moore and Maynard, 1929; Deb, 1949; Bloomfield, 1953). The latter two showed that *circa* 30–40% humus: ferric oxide is sufficient at low *p*H to keep the iron in solution. Naturally, much literature occurs on the enrichment of iron in B horizons of podzols, but this enrichment is not considered in the present study.

The iron is leached from the top horizons by the influence of the organic matter. If the profile is free-draining such material as is rendered soluble could be removed quite quickly. Even in the strongly developed podzols, a quick calculation reveals that there is insufficient iron present in the iron pan to account for the total amount of iron which would have existed in a total surface soil layer when the profile was young or immature. In the surface horizons, the iron which

is readily soluble is quite probably that which has been acted upon by the humus, and this material is therefore easily extracted by Dion's method (1944). The high iron content at depth (C horizon) is believed to be due to a simple leaching of the parent material with consequent removal of alkalis and subsequent elevation of the sesquioxide percentage.

(2) *Titanium*

The titanium content of the clays and silts has come in large part from breakdown of ilmenite and titaniferous iron ore, and in some smaller part from the biotite. It follows iron in its behaviour in the profile, thus it increases in the finer fractions and also with depth. It appears, therefore, that the same processes responsible for removal of iron are also operative on titanium. Once the titanium was in solution or colloidal dispersion, it could be camouflaged in the iron-bearing minerals for iron and titanium have somewhat similar ionic sizes.

In Profile 1 there is good evidence that the titanium content is present as anatase. Ilmenite on weathering gives as a decomposition product a whitish coloured compound termed leucoxene. The x-ray diffraction photographs of this material are often similar to those of anatase, and leucoxene is therefore sometimes believed to be anatase in a fine state of division. In Profile 1 there were several lines in powder photographs of the clay fractions, which could only be explained by the presence of anatase. Dunnington (1891) suggested that the titanium content of clay was present as ilmenite. Arsandaux (1913) working on bauxites suggested titanium was present as an amorphous metatitanic acid $TiO_2 : H_2O$. Lacroix (1913) working on laterites also postulated the presence of titanium as a hydrated form (metatitanic acid and also orthotitanic acid, $TiO_2 : 2H_2O$). Robinson (1914) suggested the titanium content was present as rutile after the analogy of rutile needles in quartz, but noted that the quartz content of fine fractions decreased. Joffe and Pugh (1934) suggested the titanium was present as ilmenite or possibly a phosphate, $Ti(HPO_4)_2$. They stated that titanium ions moved at low *p*H values and humates kept the titanium in solution; hydrolysis they suggest gives rutile. Fujimoto, Sherman and Chang (1948) recorded anatase and ilmenite in a ferruginous latosol profile, and suggested that as the titanium was concentrated in the A_2 horizon it must move, probably as colloidal titanium dioxide or titanic acid. Tanada (1952) suggested a titaniferous base exchange complex in the colloidal fractions of some Hawaiian soils.

In the profiles studied the titanium is placed as anatase, but certainly some is amorphous, and this is more especially true of those profiles developed under cooler conditions. Actually both iron and titanium show greater tendency towards crystallinity with increasing temperature of soil formation, the iron as haematite, and the titanium as anatase.

The movement of titanium in the profile is probably accomplished by a preliminary hydration of the titania, this hydration is no doubt effected more easily by the action of the humic acids, but considering the very insoluble nature of the oxides such a process would of necessity be extremely slow. It is believed that it is this hydrated titanium dioxide which is removed by the nascent hydrogen method and expressed as free titania in this paper.

Conclusions

The results obtained upon the samples investigated demonstrate a rise in percentage of iron and titanium oxides with a decrease in grain size. The increase in quantity with depth is believed to be due to the enrichment by a geological weathering process, which entails removal of alkalis and alkaline earths and hence enrichment in sesquioxides. The decrease in total amount of the latter in the surface horizons is related to the solvent influence of humus and organic acids upon the sesquioxides. For this same reason the amounts of "free" sesquioxides, as determined by the Dion method, are higher in the surface layers than in the lower horizons. If a precipitation does occur at depth in the soils studied, then a strong cementation must occur, for the sesquioxides are stable to chemical attack. It seems more probable therefore that they are removed from the profile to a large extent if it is free-draining.

The stability to chemical attack of part of the sesquioxides may well indicate that the material is present in two forms. It seems possible that the material left behind by leaching out of alkalis, and alkaline earths may be more resistant to chemical attack than that which has undergone reaction with humus or similar solvent material, for material from the iron pans resulting from solution and precipitation is fairly readily soluble. This hypothesis is advanced here as an explanation of the observed phenomena.

In the case of a poorly drained soil, different conditions could arise for here the material could not dry and therefore possible immobilization of iron and titanium by dehydration would be small. The results of Glentworth and Dion (1949) on such soils certainly indicate a greater mobility of iron under these conditions.

The iron is believed to travel as a stabilized sol, whereas the mechanism of the titanium translocation must be a preliminary hydration and then subsequently a solution.

The data raise the interesting point that if sufficient humus exists, lateritic development must of necessity be very slow.

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